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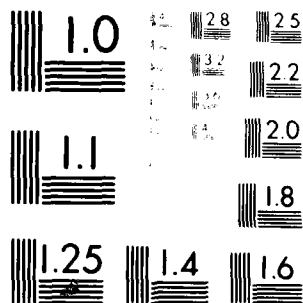   FEB 81 B LUX, G JANGG, H DANNINGER   DA-ERO-78-G-086
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Tungsten powder metallurgy,   sintering regimes,
mechanical properties,   metal additives

20. ABSTRACT (Continue on reverse side If necessary and Identify by block number)

Extensive studies of the effects of various sintering parameters and many substituents on the mechanical properties of tungsten test samples produced by powder metallurgical methods have been completed. As final result of this work it can be stated that the influence of the sintering parameters is much more pronounced than that of the purity of the starting W powders, if they are in the normal range of a good high quality industrial product. For both absolute values and reproducibility of →

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Final Technical Report

The influence of chemistry and various fabri-
cation parameters on the properties of tungsten
heavy metals

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Institut für Chemische Technologie Anorganischer Stoffe
TU Vienna

Vienna, Feb.1981

INTRODUCTION

The final aim of this two years' project was the
improvement of tungsten heavy metals, especially
with regard to two of their mechanical properties,
of which tensile strength and elongation were the most
important.

The improvements were to be achieved by investigating
the influence of the production parameters, esp.
sintering cycle and sintering parameters, and the
effect of impurities, both in the starting W-powders
and the binder phase, on the mechanical properties
of the sintered samples. To recognize even slight
effects with certainty, the sintering had to be performed
exactly according to the pre-set sintering cycle, so
that an excellent reproducibility of the results could
be achieved.

During the first year's work on this project, the
investigations concentrated mainly on the fabrication
parameters of heavy metals with sufficiently good
mechanical properties. The influence of grain size and
grain size distribution of the W-powders as well as the
effect of different pressing lubricants on the compacti-
bility of the powder mixtures were thoroughly examined.
It was found that powders with a grain size of ~3 μm
give the best results; after addition of 1% camphor and
a granulation treatment, the powders can be compacted
without difficulty at pressures up to 5 t/cm^2.

Early sintering experiments showed that a minimum
temperature of 1460°C is necessary for the production
of nonporous samples; higher W-contents (95 and 97%W)

require a somewhat higher sintering temperature. A sintering
time of 30 min was found to be optimal for all compositions;
unwelcome grain coarsening could thus be avoided.

The sintering tests also showed the decisive importance
of a thorough pre-reduction treatment of the samples
before sintering. Poor de-oxidation resulted in extremely
low ductility and causes a decrease and a wide scatter
in tensile strength values. With a uniform composition
of 90 wt% W, 6,7 wt% Ni, 3,3 wt% Fe, carefully pre-
reduced   samples showed tensile strengths of up to
1000 N/mm^2 and elongations of up to 27% with surprisingly
good reproducibility; even with heavy metals containing
95% W, elongation values of 13% could be obtained. The
addition of reducing metals to the binder as Cr and V,
did not render the pre-reduction unnecessary; the
elongations thus achieved were only half those of pre-
reduction samples.

After a sintering cycle had been found that resulted in
good mechanical properties obtainable with a very high
rate of reproducibility, further investigations into
production parameters and also into the influence of
impurities became possible during the second year. Of
the many possible directions of research, the most promising
were:

1) Simplification of the sintering cycle:
   The sintering cycle most effective in our experiments
   is not easily reproducible in industrial furnaces;
   a sintering cycle consisting of several stages at
   fixed temperatures could be controlled more easily.
   Optimization of the duration and temperature of these
   steps, therefore, was regarded as a main target for
   the investigations.

2) Sintering and heat treatments in various atmospheres:
   Several authors claim that heat treatment of the
   sintered heavy metals in hydrogen (1) or under vacuum
   (2,3) is essential for the production of W heavy
   metals with high tensile strength and elongation. Our
   experiments (see First Annual Report) had shown that
   samples cooled slowly from sintering temperature to
   500°C had almost twice the elongation of rapidly
   cooled samples. It was to be investigated if this
   discrepancy was caused by the sintering atmosphere
   or if it was an effect inherent in the system W-Ni-Fe.

3) Addition of small amounts of other metals to the Ni-Fe-
   binder:
   In the literature, many metals have been used as
   additives to W heavy metals. These additives were
   usually in the range of several wt% of the mixture
   and often comprised metals whose prices were, of have
   now become rather high (e.g. Co). It seemed promising,
   therefore, to reduce the content of those metals,
   without greatly reducing the desirable effects.

4) Investigations into the influence of trace impurities
   contained in the starting W powders:
   As there are many types of W powders, which, due
   to their different origins, contain different amounts
   of impurities, knowledge about positive or negative
   influences of impurities would be helpful in the selection
   of W-powders for the production of W heavy metals. Further
   definitely positive influences of certain impurities
   might recommend the doping of the W powders with these
   elements.

Summary of the experimental work performed:

1) <u>Description of the starting materials</u>:

The W powders used in the experiments were specially
prepared for us and supplied by local tungsten manufacturer.
Requested powders with various doping additives were
produced. Tab.1 shows the specifications of the powders
regarding chemical purity and mean grain size as
determined by Fisher SSS; these results are in good
agreement with the grain size distribution spectra
determined by standard sedimentation methods (see
appendix); these data were supplied by the manufacturer
together with the powders. Normally the average grain
size is near 3 μm, although a few powders are considerably
coarser, up to ~10 μm. These powders have a somewhat
broader grain size distribution spectra than the finer
ones. Chemically, the W-powders are very pure. Except
for the doping additives, the impurities are in the
range of <20 ppm, with several elements <10 ppm. From
the difference between the amount of doping elements
added before reduction of the WO_3 and the analyses after
reduction it is evident that some elements, e.g. Na,
evaporate to a very large extent during reduction. This
behavior has also been reported by Lassner et al.(4).

SEM-photos(Fig.1-20) clearly show the quite similar
appearance of the different W powders. There are some
differences in their tencency to form agglomerates,
and some powders exhibit more pronounced crystal facets
on the particles than others. However, only the powder
E 14W containing Al is markedly different from the other
ones, the surface of the grains being covered with
small rods and dots. Analyses have shown, that these
contaminations consists mainly of Al_2O_3.

Table 1: Chemical Analysis of the W-powder (contents in ppm)

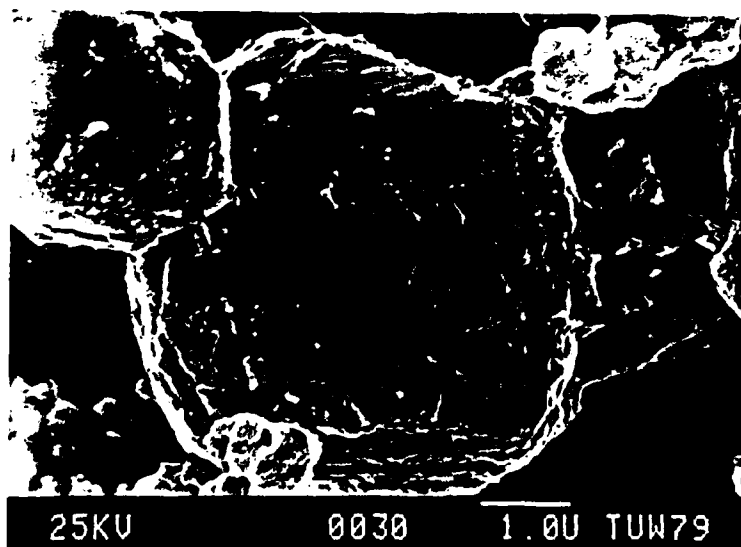|	Additive	C	O_2	P	Al	Ca	Co	Cr	Cu	Fe	K	Mg	Mo	Na	Ni	Si	V
5o3		20	240	21	<10	<10				12			<20	26	<10	<20	
E 2	250 Na	7	130	42	<10	<10				<10			<20	20	<10	<20	
E 5	250 Li	4	630	44	<10	<10				<10			<20	<10	<10	<20	
E 8	188 Ca	15	280	43	<10	220				<10			<20	<10	<10	<20	
E 11	250 B	24	760	48	<10	<10				<10			<20	22	<10	<20	
E 14	250 Al	17	470	37	288	<10				<10			<20	22	<10	<20	
E 17	100 Si	11	470	24	<10	12	<10	<20	<10	12	14	<10	<20	48	<10	96	<25
E 21	140 Na, 100 P	24	310	93	<10	<10	<10	<20	<10	<10	<10	<10	<20	24	<10	<20	<25
E 24	100 As, Sb, Bi	15	640	31	<10	12	<10	<20	<10	24	<10	<10	<20	26	12	<20	<25
E 27	100 U	11	450	29	<10	16	<10	<20	<10	<10	<10	<10	<20	18	<10	<20	<25
E 30	188 Na, 1o6 Al 113 U, 5oo F	14	220	52	64	<10				12			<20	48	<10	<20	
E 33		11	310	49	<10	<10	<10	<20	<10	<10	14	<10		14	<10	<20	
E 36	100 Na	13	240	30	<10	12	<10	<20	<10	<10	1o	<10	<20	22	<10	<20	<25
E 39	50 Na	6	270	23	<10	16	<10	<20	<10	<10		<10	<20	22	<10	<20	<25
E 45	100 Li	4	530	36	<10	<10	<10	<20	<10	<10	<10	<10	<20	<10	<10	<20	

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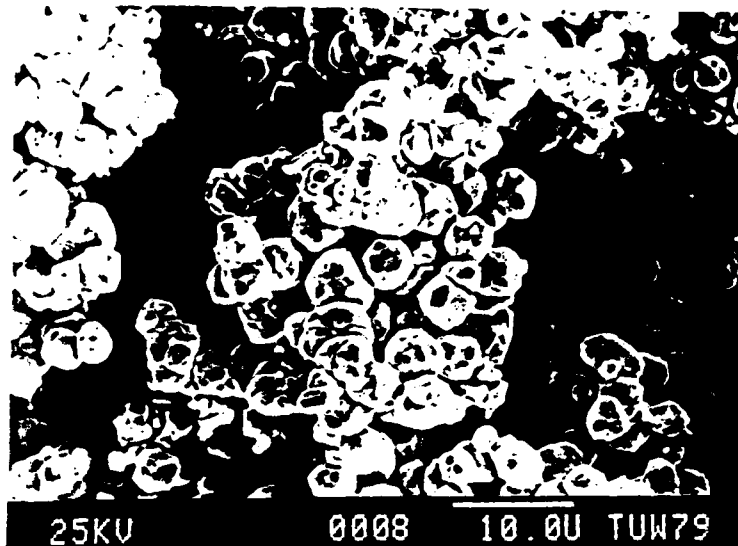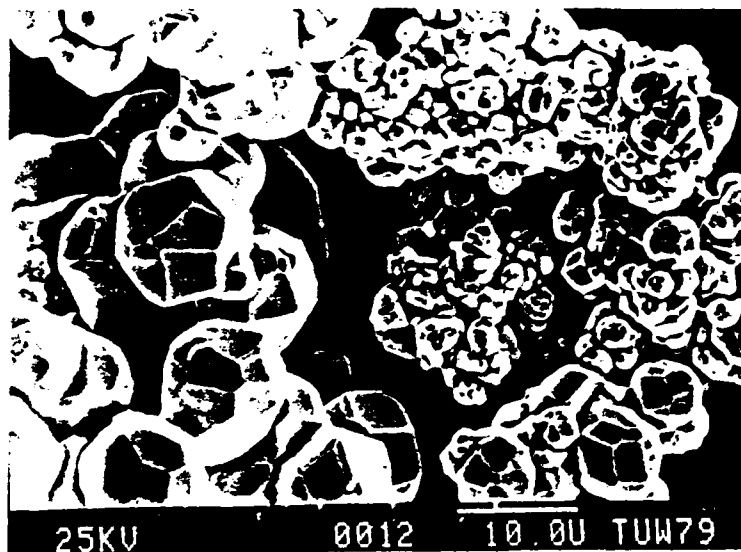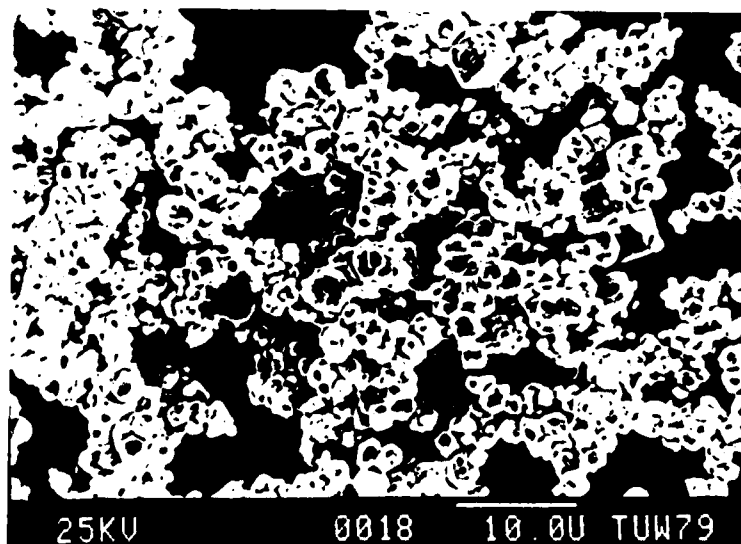
Fig.1
E2W
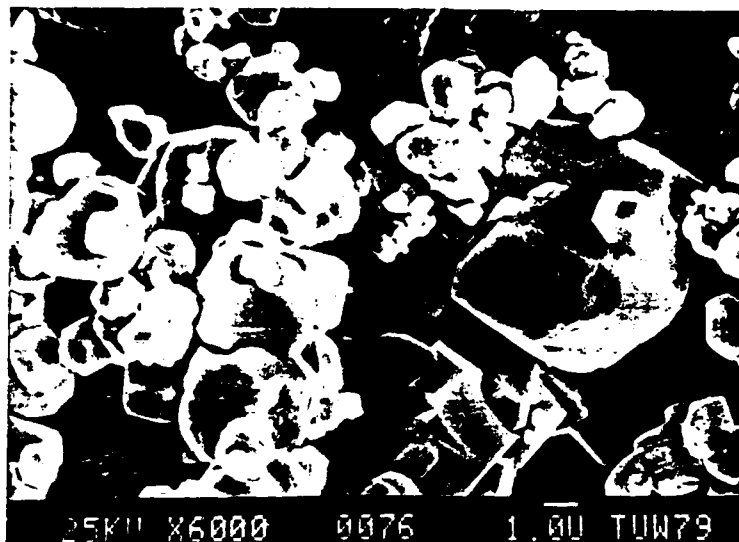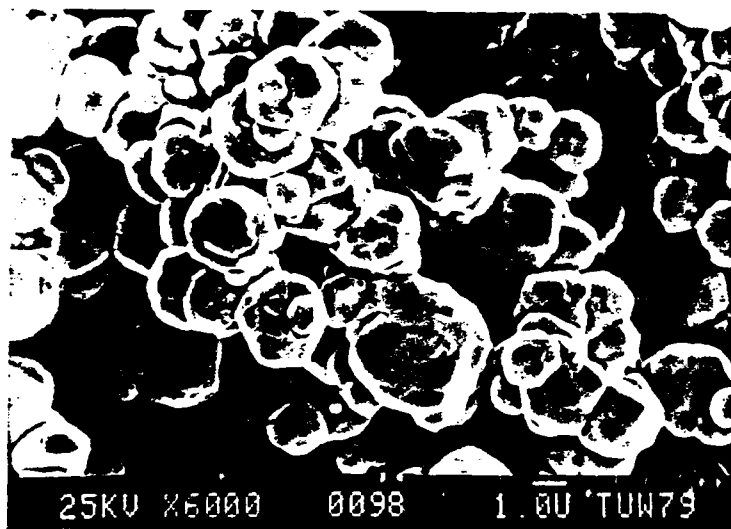

Fig.2
E5W

Fig.3
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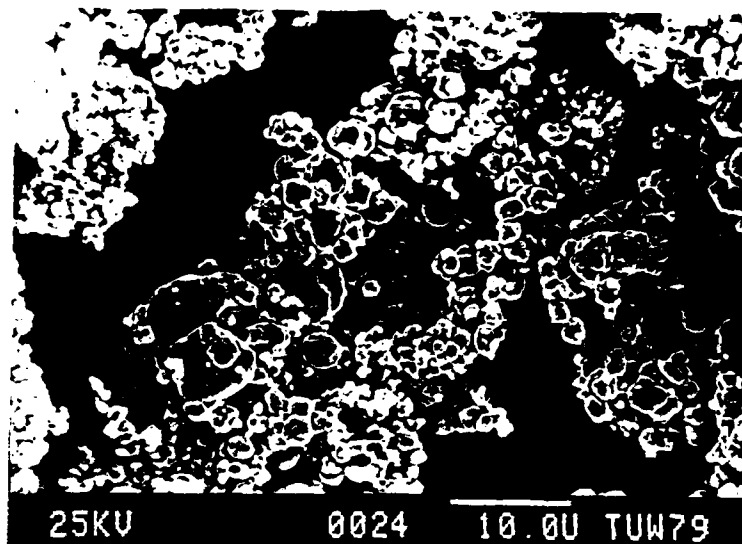
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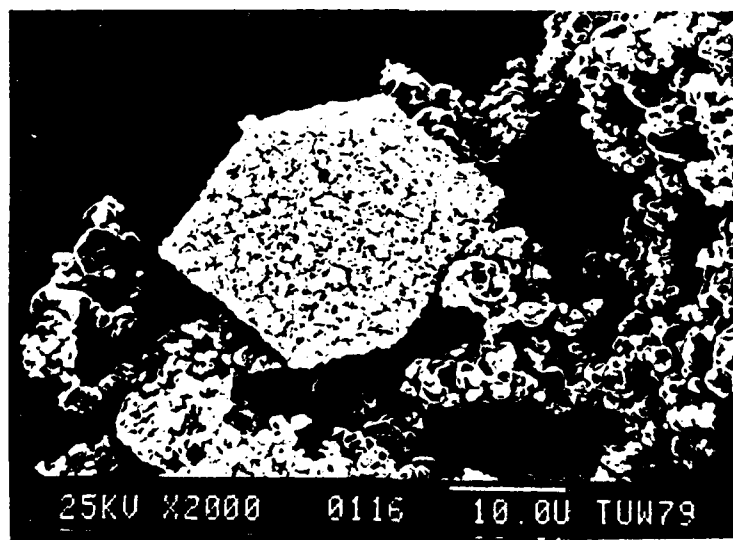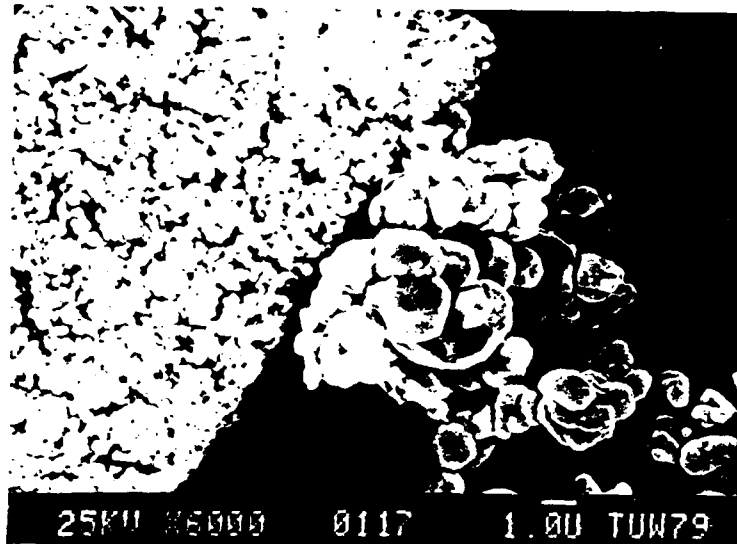E11W
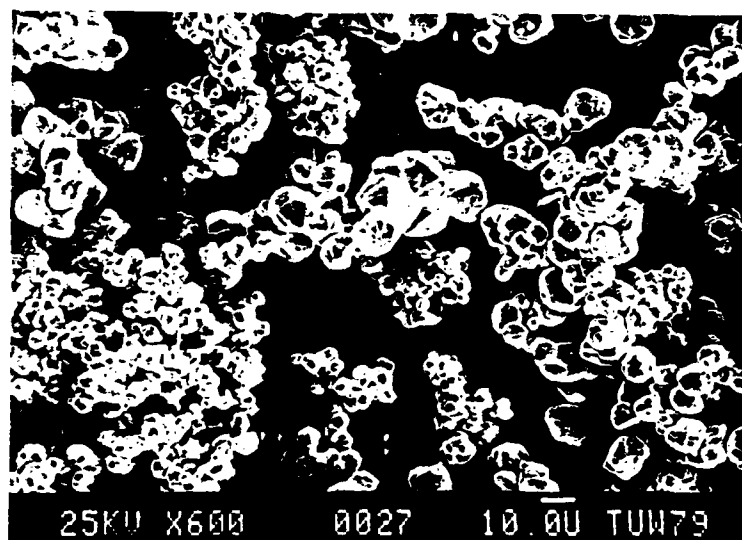
Fig.5
E14W

Fig.6
E14W

Fig.7
E17W

Fig.8
E21W

Fig.9
E24W

Fig.10
E24

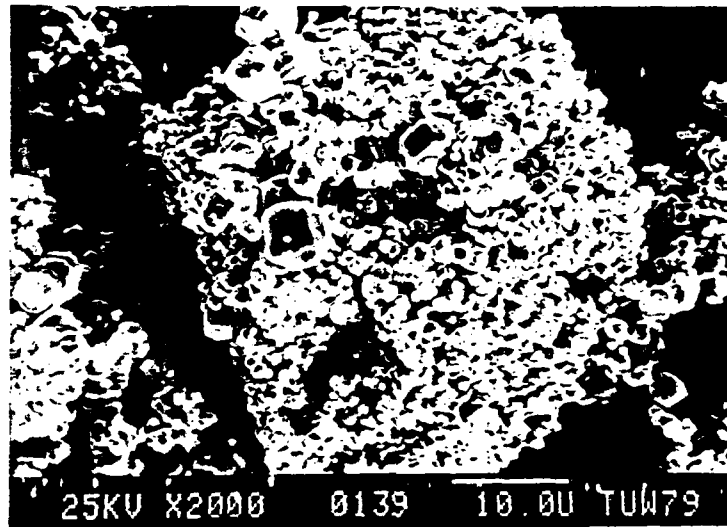
Fig.11
E27

Fig.12
E30

Fig.13
E33W

25KV   0038   1.0U TUW79

Fig.14
E36W

25KV X6000   0170   1.0U TUW79

Fig.15
E39W

25KV X6000   0134   1.0U TUW79
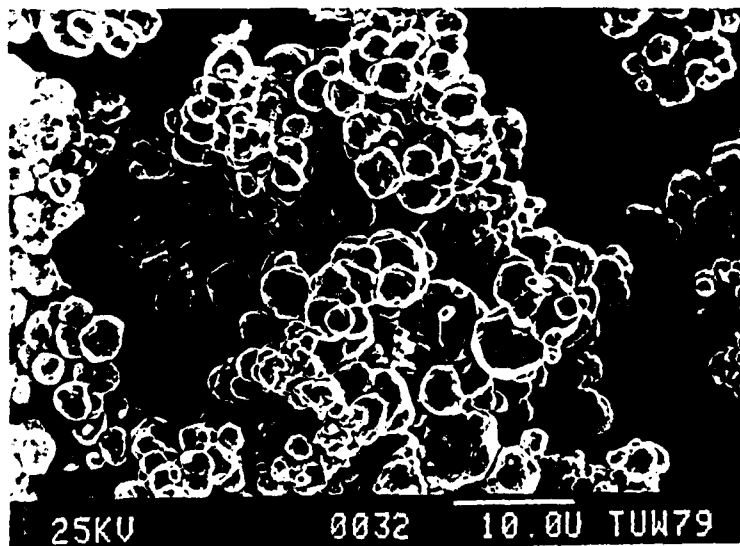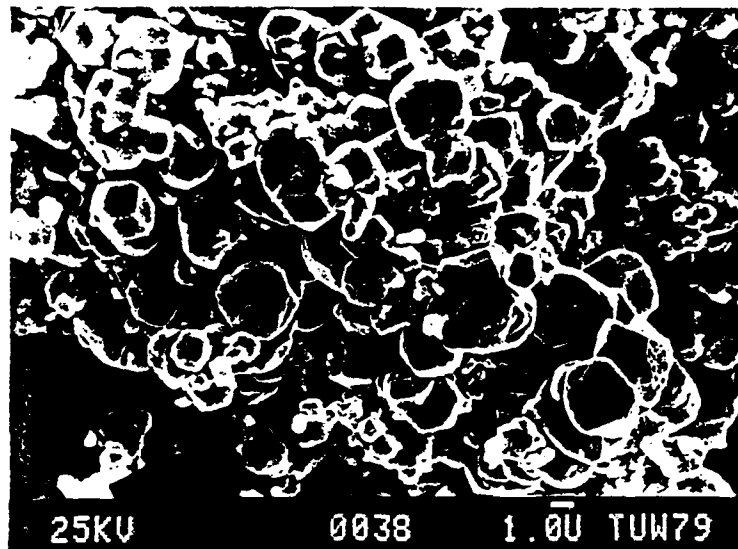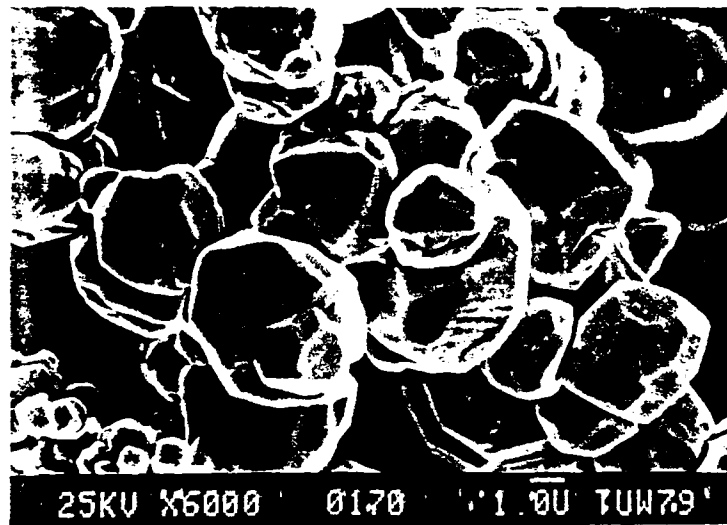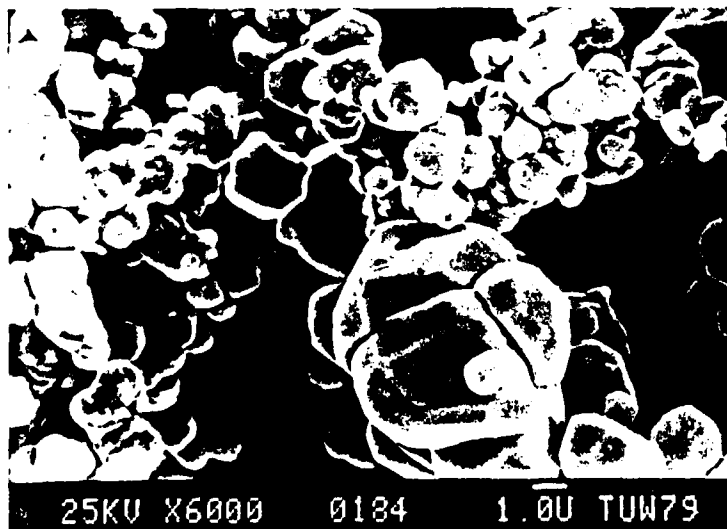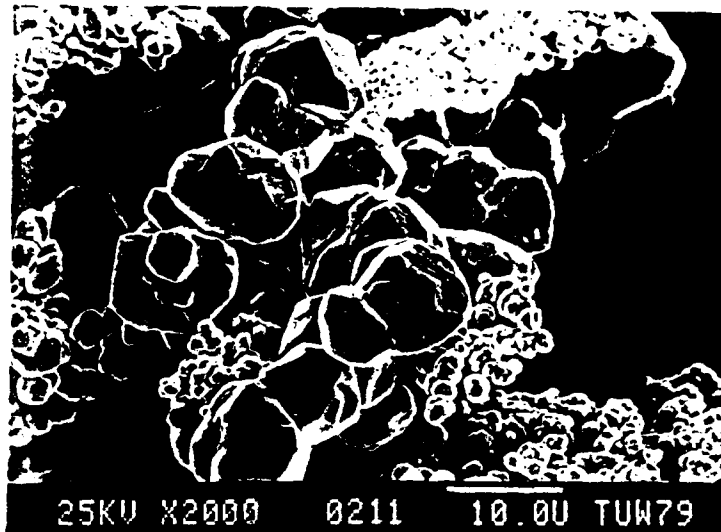
Fig.16
E45W

Fig.17
E45W
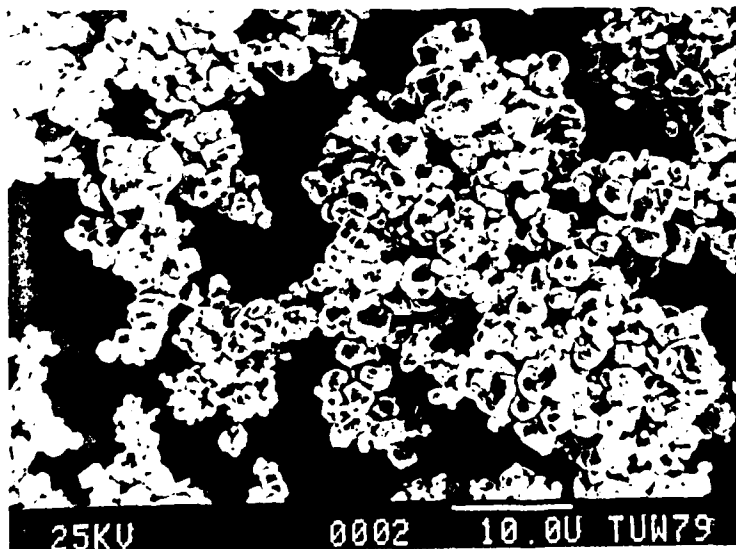
Fig.18
W5O3
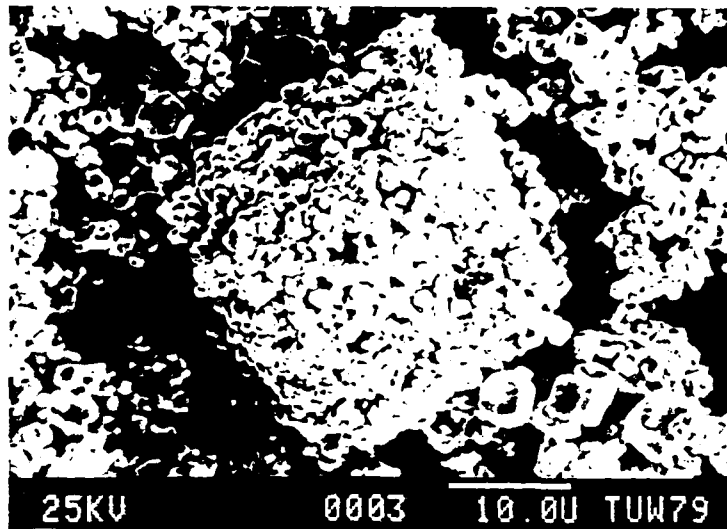
Fig.19
W5O3
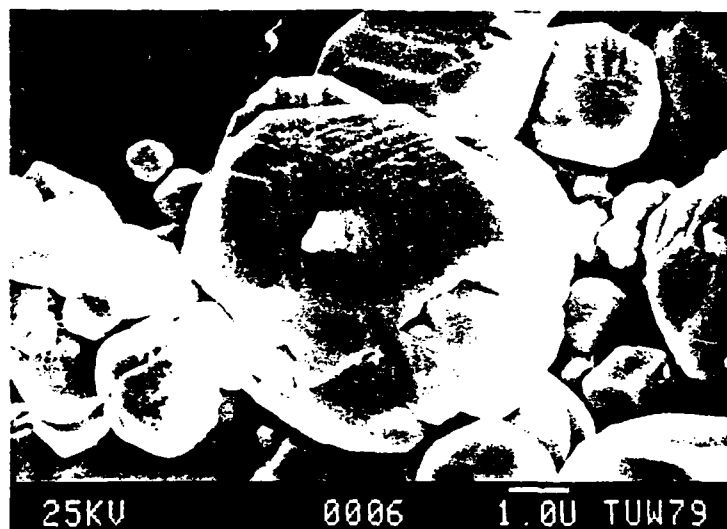
Fig.2o
W5O3

The Fe and Ni powders supplied by BASF, Germany, were
of carbonyl quality. Their grain sizes were around 5 μm,
the C-content was 219 ppm for Fe and 707 for Ni, and
the O-content was 2020 and 910 ppm respectively. The
pressing tests had shown that best results were obtained
with 1% camphor as a pressing aid; all further experiments
were carried out with this amount of pressing lubricant.

2) Preparation and testing of the samples

The green compacts were prepared as described in our
previous reports; the powder mixtures, always consisting
of 90 wt% W, 6.7 wt% Ni, 3.3 wt% Fe, were wet mixed in
cyclohexane with 1% camphor as pressing lubricant. After
3 hrs of mixing in a rotation mixer the cyclohexane was
partially evaporated; the still damp powder was then
granulated through a 0,8 mm mesh sieve and afterwards
dried thoroughly.

The powders were compacted to standard tensile strength
bars 1 sq.in. in area (MPIF Standard 10-63) in a pressing
tool with floating die to ensure uniform pressure from
above and below. Pressure was applied by means of a
150 ton capacity hydraulic press. For the compaction
of the W-Ni-Fe-powder mixtures, a pressure 5,15 tons/cm^2
was found to be optimal for giving sufficient densities
without causing pressing faults.

The green samples were sintered in a furnace with a Mo
heat conducting coil for temperatures up to 1650°C. The
furnace always was operated in a reducing atmosphere,
usually H$_2$ of technical purity. The temperature regulation
allowed the furnace to be maintained within $\pm 5^{\circ}$C of the
set temperature. This exactness was essential for obtaining
the necessary reproducibility.

The samples were transported in Mo boats, usually
8 bars per boat. To prevent them from fusing together
during sintering, the space between them was filled
with Al_2O_3 powder. The front ends of the bars were
usually left uncovered to permit the observation of
the "silberblick" effect – the first melting of the
liquid phase – when the samples suddenly become darker
than the surrounding Al_2O_3. To make it possible to
control the furnace temperature by pyrometer and to
move the boats inside the furnace without opening the
shutter, a special shutter was constructed which
incorporated a stuffing box for a long hook and as
small bulleye whose glass cover could be removed to
avoid false temperature measurements because of the
absorption of the radiation by the glass. Thus the
intrusion of oxygen into the furnace atmosphere could
be kept minimum.

After sintering, the interesting properties of the test
bars were measured. To determine the sinter compact
density, the water buoyancy method was used, which gives
more accurate results than the Hg displacement method.

The hardness was checked on a Vickers tester, with a
weight of 62,5 kp. Whenever promising, microhardness
values were determined on metallographic sections to
check the difference in hardness between grains and
binder phase.

A tensile tester with a maximum load of 30 kN was used
for the determination of tensile strength and elongations,
the gage length being 25 mm.
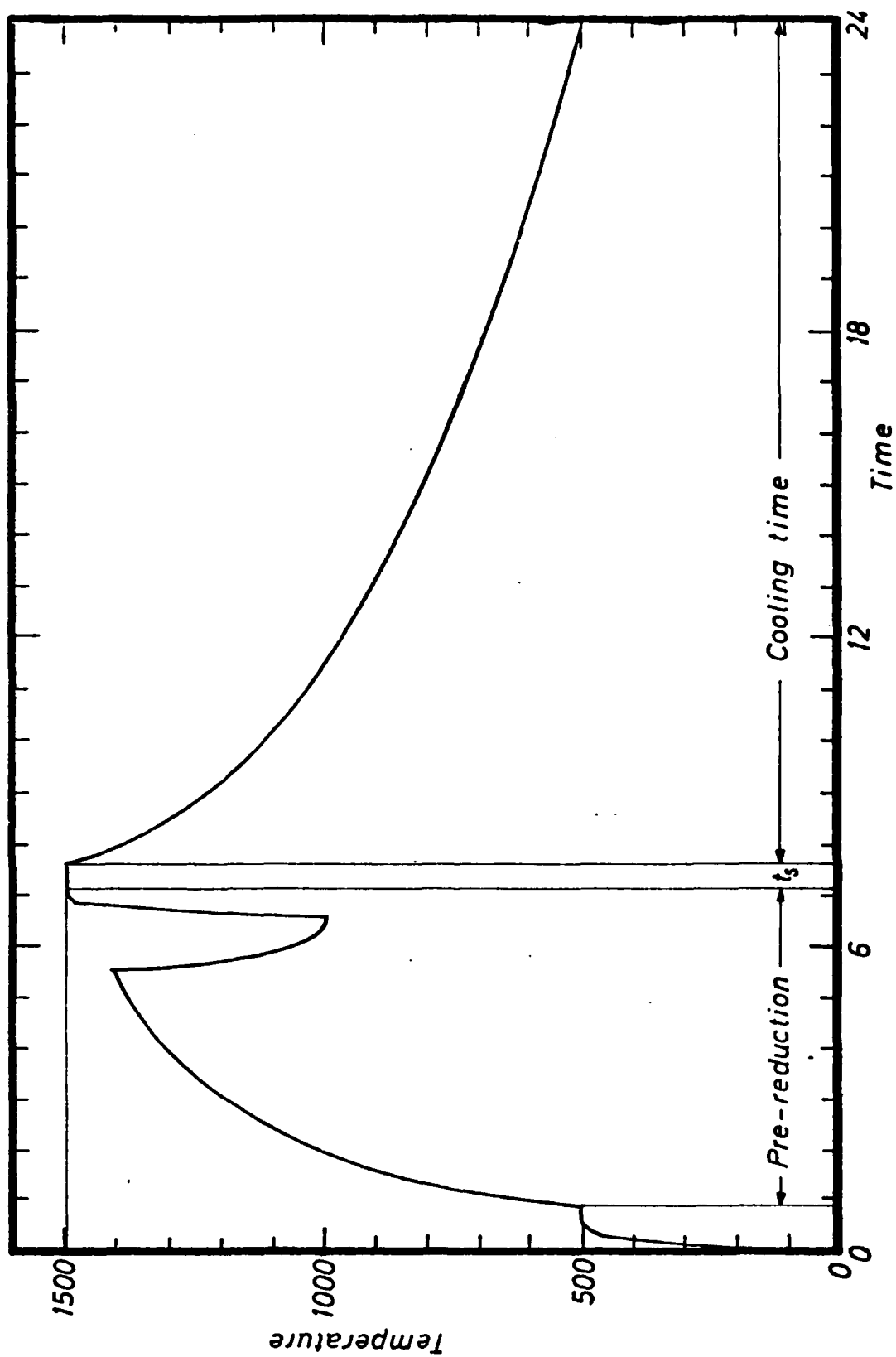
Fig.21: Temperature-time-diagram for the standard sintering cycle

3) Variation and simplification of the sintering cycle:

The sintering cycle found best in our experiments was
easily reproducible in our furnace, but was adapted
for the special heating and cooling characteristica of
this laboratory Mo-furnace. To make our experiments
reproducible in industrial furnaces, it was recommendable
that a sintering cycle consisting of steps at constant
temperature levels especially in case of the pre-
reduction, be found. For this purpose, the individual
steps of the sintering cycle were evaluated more carefully.

3.1 Removal of the pressing lubricant

Although earlier experiments had shown (see First Annual
Report) that embrittlement by carbon did not normally occur
in W heavy metals, it seemed possible that, for example,
a too rapid heating of the green compacts would lead to
decomposition of the camphor thus contaminating the alloy
with carbon. To evaluate this possibility, several de-
waxing treatments were tried: first of all, a normal de-
waxing by shoving the samples into the heating zone of the
furnace at 500°C, where they remained for 60 min; then
the sintering was carried out as usual (Fig.21). Second,
a very slow de-waxing was tried where the samples were
pushed stepwise into the furnace, thus requiring 60 min
to reach 500°C. The third de-waxing was a shock treatment:
the samples were pushed immediately into the 1200°C heating
zone. Further treatment and sintering were performed as
usual. In this last case comparison samples without any
pressing lubricant at all were also sintered together with
the usual 1% camphor green samples to determine any detrimental
influence of the pressing lubricant (Tab.2).

Table 2: Mechanical properties of samples with different
de-waxing treatments (W 503/79); 3 hrs pre-reduction
at $1200^{\circ}C$; $1490^{\circ}C$, t_s 30 min; average values
from 4 samples.

	Density g/cm^3	σ_B (MPa)	Elongation (%)	Hardness 62.5
slow de-waxing	17,072±0,005	734±14	2,1±0,6	289±4
nomal de-waxing	17,05 ±0,01	930±18	23,0+1,3	293±3
shock de-waxing (1% camphor)	17,051±0,02	1007±12	20,5±2,4	292±2
no lubricant	17,040±0,01	997±10	20,2±2,0	288±1,5

As seen in Tab.2, the most careful de-waxing process
resulted in the most brittle products, while the shock
de-waxing did not cause any deterioration of the mechanical
properties; In this case, samples with and without camphor
showed the same elongations after sintering.

Presumably in the slow de-waxing process the lubricant reacts
with the metal powder before it has completely evaporated;
the resulting layers of WC inhibit the wetting of the
W grains by the binder in the following sintering process.
In the normal de-waxing and particularly in the shock treatment
the pressing lubricant evaporates before a significant
reaction is possible.

Formation of pores or cracking did not occur; the green
porosity of more than 30% is sufficiently high to permit
easy evaporation of the camphor evaporate without obstacles.

It is conceivable, however, that with larger samples difficulties with de-waxing might be encountered; Industrial practice usually compacts heavy metals isostatically without adding pressing lubricant. It might be of interest, too, to produce heavy metals by die compaction without pressing lubricant. To check the behavior and properties of such heavy metal products a series of tests using samples with and without pressing lubricant was carried out. The composition of the mixtures used was the usual 90% W, 6.7% Ni, 3.3% Fe with standard W powder 503/79 (3.05 μm). As could be expected, the compaction of the powder mixtures without pressing lubricant was considerably more difficult; uniform filling of the powder in tne die was of decisive importance to avoid pressing faults (Tab.3).

Table 3: Mechanical properties of samples without pressing lubricant. Standard powder W503/79; sintering Cycle 2 (slow heating and cooling). Average value from 4 Samples. In brackets samples with 1% camphor. Green density at 5,15 ton/cm^2: 10,785 g/cm^3 (11,52 g/cm^3)

	Density (g/cm^3)	Hardness 62,5	σ_b (MPa)	% Elongation (%)
Cycle 2; 1475°C	16,991±0,04	303±4	838±9	0,55±0,3
	(17,073±0,01)	(295±4)	(925±14)	(23,7 ±3,2)
Cycle 2; 1490°C	17,062±0,016	298±3	1005±4	22,6 ±1,4
	(17,046±0,02)	(293±3)	(962±13)	(24,6 ±1,1)
Cycle 2; 1510°C	17,030±0,02	293±4	980±8	24,2 ±2,6
	(17,062±0,16)	(285±3)	(923±11)	(19,7 ±1,2)[x]

x) strongly rounded edges

Samples without pressing lubricant apparently must be sintered at a considerably higher temperature; densities of ~100% and sufficient tensile strengths and elongation were obtained here at temperatures of 1490°C and 1510°C as compared to 1470°C-1490°C for normal specimens with 1% camphor. The mechanical properties were within the usual range; as the handling of green compacts pressed without camphor requires much care and since no difficulties with lubricant bake out were encountered, it was decided to use pressing lubricant for all further experiments.

Pre-reduction of the green compacts:

For simplification of the sintering cycle, we decided to carry out pre-reduction of the green compacts as fixed temperatures for a given length of time. Green compacts were de-waxed at 500°C for 60 min, then the furnace was heated up to pre-reduction temperature and the samples were pushed in. After 3 hrs, the samples were pulled into a cooler zone, the furnace were heated up to sintering temperature and the samples were pushed back into the hot zone for sintering. Afterwards the furnace was switched off and the samples remeined there for cooling (cooling rate see Fig. 21).

Table 4: Mechanical properties of heavy metals pre-reduced
for 3 hrs at different temperatures. Sintered
30 min at 1470°C, slow cooling (Average values
from 4 samples)

Pre-reduction temperature	Density g/cm^3	Hardness Hv 62,5	σ_B MPa	Dehnung %
800	17,111	289	720±19	3,1±1,5
1000	17,122	302	940±21	16,3±2,3
1100	17,109	307	947±16	20,9±1,4
1200	17,102	299	954±9	22,1±0,8
1300	17,122	296	917±6	13,8±1,4
1400	17,091	293	895±24	5,0±3,2

The tests show that temperatures below 1000°C are somewhat
too low for satisfactory pre-reduction; probably the
reduction rate is not high enough. The optimal pre-reduction
temperature seems to be in the range of 1000-1200°C;
elongations of >20% can be obtained without difficulties.
The very low elongations observed after pre-reduction
temperatures of 1300°C or more can be explained by the
fact that at temperatures relatively close to the melting
point of the liquid phase the solid phase sintering
proceeds so fast that the pores close up before complete
de-oxidation can occur. Samples pre-reduced for 3 hrs
at 1300°C and taken out of the furnace had shrunk almost
to the size of liquid phase sintered samples.

Further support for this explanation comes from the fact
that samples pre-reduced at 1000-1200°C pulled afterwards
into the water-cooled zone of the furnace and then sintered
resulted in very low elongations, while samples pre-reduced,
by heating them slowly from 500 to 1400°C (Fig. 24) suffered
no damage by this intermediate cooling. In this case the
reverse effect occured: during the cooling process the

water vapor present in the furnace atmosphere oxidized
the heavy metal; samples with open pores were also
contaminated in the interior, which rendered the pre-
reduction treatment ineffective. Samples with closed
pores were re-oxidized on the surface but remained intact
in the interior. Therefore, the possibility of re-
oxidation after the reduction must also be carefully
excluded, otherwise embrittlement will be encountered
even after thorough reduction.

Pre-oxidized samples

To test the effectiveness of the pre-reduction treatment
as shown in Fig.21, even in the case of heavily oxidized
samples, several standard green samples were oxidized
intentionally by heating them in air for 15 min at $420^{O}C$
until they showed yellow brown and blue colors on the
surface. Afterwards some samples were put into the furnace
and slowly heated from 500 to $1400^{O}C$, the treatment
lasting for 6 hrs. Other samples were pushed immediately
into the heating zone and cooling were carried out as
usual (Tab.5).

Table 5: Properties of sintered samples heated up to
sintering temperatures at different rates
(green compacts preoxidized) Average values
from 4 samples. (W 503/79 , $1480^{O}C$, t_s 30 min,
slowly cooled)

	Density (g/cm^3)	Hardness Hv 62,5	σ_β (MPa)	Elongation (%)
rapid heating within 30 min	$16,871\pm0,12$	286 ± 7	784 ± 17	$3,6\pm0,3$
slow heating within 6 hrs	$17,080\pm0,01$	299 ± 3	998 ± 9	$22,4\pm1,3$

All samples sintered without pre-reduction exhibited large swellings, high porosities and extreme brittleness. As the pressing lubricant had been removed by the oxidizing treatment, the swelling and pore formation must have been caused by evaporation of volatile compounds in the heavy metals, probably tungstic oxides.

The extremely low tensile strengths and elongations of those samples are caused by the poor interphase strength between W-grains and binder. SEM investigations showed clearly the intergranular fracture; the surface of the grains is covered with dark blotches which are most probably oxidic contaminations inhibiting the wetting between binder phase and W grains (Fig.22). Similar phenomena were also observed in earlier investigations (First Annual Report) but always on samples with poor elongations.

On the other hand, the properties of the oxidized and pre-reduced samples were quite similar to those of samples not subjected to oxidizing treatments. The samples were fully dense and tensile strength and elongation reached a very satisfactory level. Investigations of the fracture surface revealed the characteristics of highly ductile samples: transgranular fracture, excellent interphase strength and severe deformation of the binder (Fig.23). It can be concluded, therefore, that thorough pre-reduction treatments also give excellent results in the case of heavily contaminated heavy metals; even heavily oxidized powders may be used for production of these alloys, if a proper pre-reduction treatment is carried out.
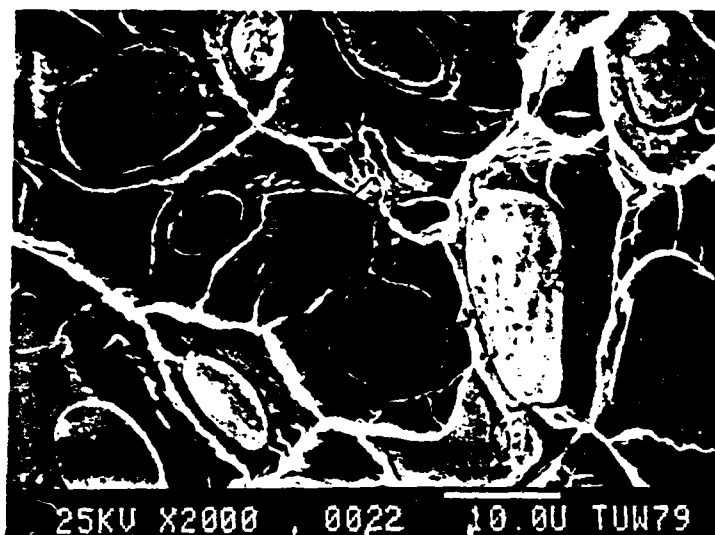
Fig.22: No pre-reduction before sintering
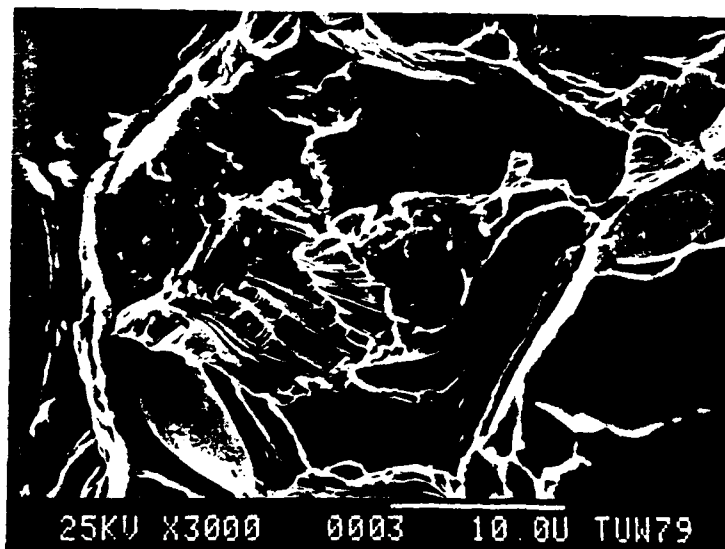
Fig.23: Pre-reduction as shown in Fig.21

Fracture surfaces of W heavy metals intentionally oxidized
and then sintered for 30 min at 1470°C

3.4 Influence of the dew point

Regarding the detrimental effect of low O-contents in
W heavy metals, the investigation of the influence of
oxygen in the H_2-atmosphere, expressed as dew point, was
an interesting problem. For the tests, a Casella dewpoint-
meter was available.
The gas leaving the furnace had a dew point of 5-15°C.
It was suspected that either a leak in the furnace or
impure H_2 was responsible for this high H_2O-content.
Careful examinations revealed, however, that this high
dew point was due to a high temperature reaction of H_2
with the ceramic lining of the furnace to form H_2O. This
is illustrated by Fig.24, which shows the dew point as a
function of the furnace temperature. The regulation of
the dew point was possible only by changing the flow of
hydrogen through the furnace, which lowered the dew point
to ∿ 0°C.

A larger series of sintering tests was performed at
different dew points, but at the same sintering conditions.
Fig.25 shows the more or less statistical relationship
              between dew point and elongation. Up to a dew
point of + 5°C elongations of more than 20% are obtained;
at higher dew points, the probability of obtaining lower
elongations is markedly increased.

3.5. Cooling after sintering:

Several authors (1,3) mention that the cooling rate influences
the mechanical properties of W heavy metals. R.V.Minakova et al
(5) cooled heavy metals slowly to certain temperatures and
then quenched them; they found that the samples were more
ductile, the lower the temperature from which they were
quenched . Within this project, earlier investigations showed
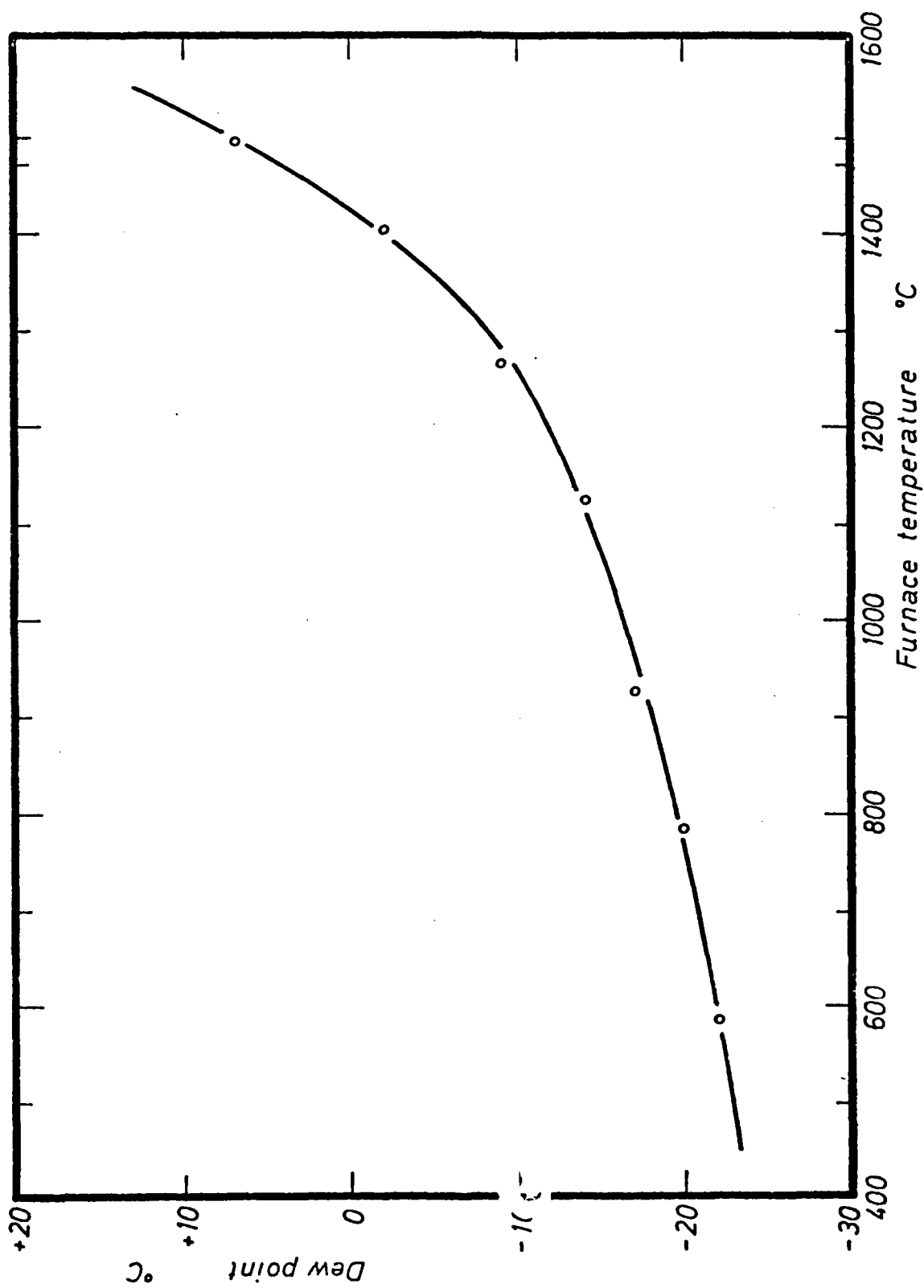
Fig.24: Dew point of the H$_2$ atmosphere as a function of the furnace temperature
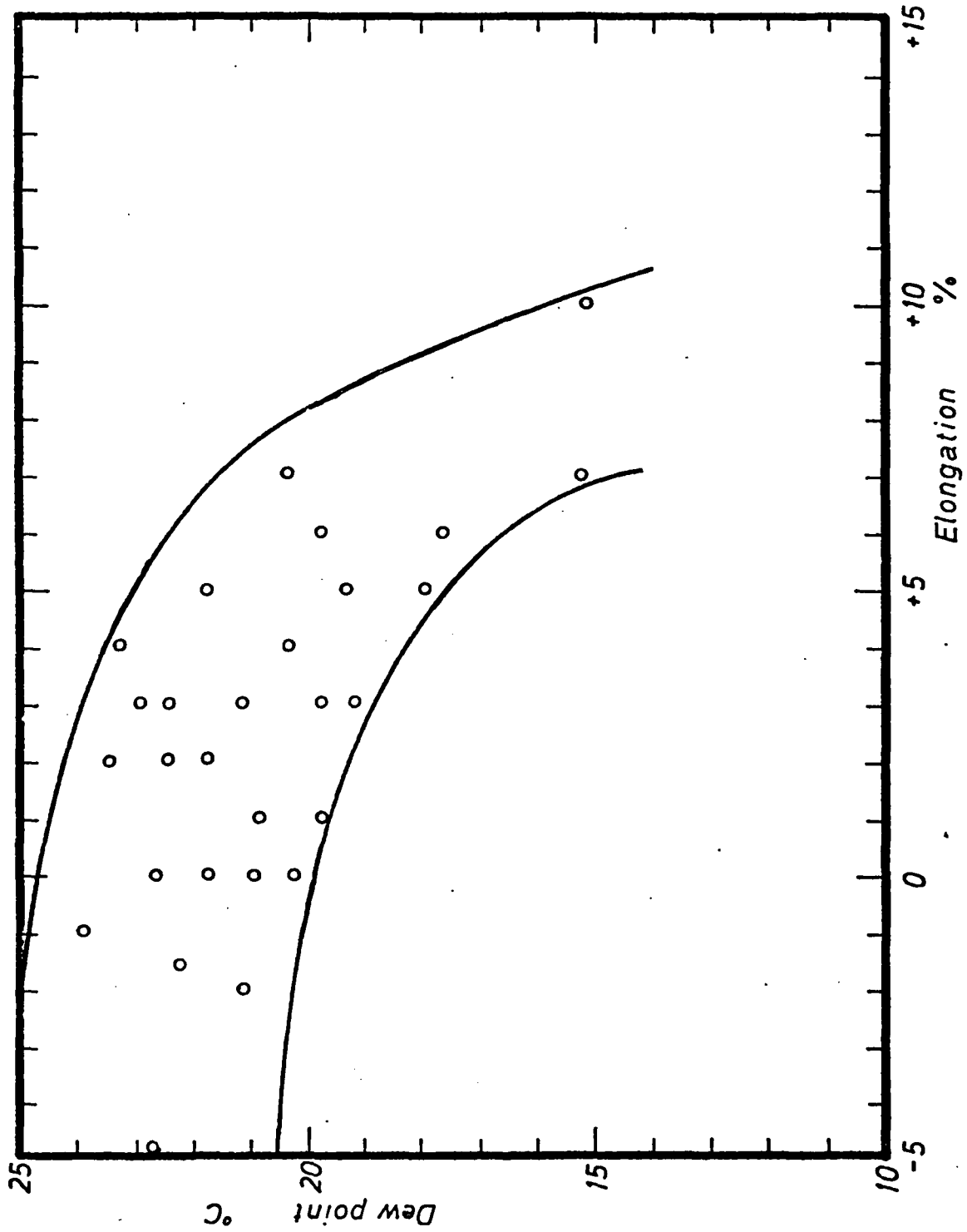
Fig.25: Elongation of sintered samples as a function of the dew point during sintering

that slow cooling in the furnace after sintering doubled
the elongation in comparison to rapidly cooled samples.
Even in the furnace, however, the samples are cooled rather
quickly in the first minutes. It might be of interest
to lower the cooling rate during the inital stage of
cooling (solidification of the liquid phase). The samples
used for these tests were of standard composition and
were de-waxed, pre-reduced and sintered as usual (fig.21).
Then the furnace was cooled within 30 min from 1475 to
$1415^{O}C$, afterwards the samples were cooled to room
temperature, either in 14 hrs or in 30 min or, by
quenching in water, in a few seconds.

Table 6: Properties of sintered samples cooled by different
procedures. Pre-reduction as in Fig.21, sintered
30 min at $1475^{O}C$.

Cooling	Density g/cm^3	Hardness Hv 62,5	σ_B MPa	Elongation (%)
1475-1415°C in 30 min,	17,115	311	965	22,8
then slow cooling	17,108	308	971	21,3
in the furnace	17,102	314	958	20,9
	17,088	304	981	23,3
1575-1415°C in 30 min,	17,102	299	924	19,6
then quenching in	17,108	303	931	20,2
water	17,112	296	916	18,7
	17,094	298	920	18,8
1475-1415°C in 30 min,	17,094	303	924	18,0
then rapid cooling to	17,092	298	926	19,2
room-temperature in	17,101	306	911	19,8
30 min.	17,088	304	930	17,3

These modified cooling treatments did not result in
superior mechanical properties. When cooled in the furnace
within 14 hrs, the samples were roughly comparable to those
sintered in the usual way (Fig.21), otherwise a certain
decrease in tensile strength and elongation was observed.
It is evident, however, that samples cooled within 30 min
from $1415^\circ C$ are much more ductile than those cooled in
the same manner from sintering temperature; the elongation
increased from 12% to 18%. To further investigate this
phenomenon, a series of heat treatment tests was carried
out.

3.6   Heat treatments:

In the literature, heat treatments are proposed to remedy
embrittlements in W heavy metals encountered after sintering,
either to remove embrittling phases (1) or to suppress
the embrittling influence of hydrogen (2,3). Within this
program, the goal was the further improvement of samples
with already satisfactory ductility i.e. 24% elongation
for 90% W . Standard samples 90% W (503/79), 6,7 Ni, 3,3 Fe
were subjected to the usual sintering treatment (fig.21)
and then heat treated at different temperatures in H_2
or N_2. Afterwards they were either cooled down in the
furnace or quenched in water. Tab.7 shows the results.
For comparison purposes the properties of samples sintered
in the same batch but not subjected to heat treatment
are shown in each group; again the excellent reproducibility
of the properties is evident.

Table 7: Properties of samples sintered as in fig.21
and then heat treated. Sintered at $1470^{\circ}C$ for
30 min; heat treated for 30 min (Average values
from 4 samples)

Temp.of heat treatment $^{\circ}C$	Cooling	Density g/cm^3	Hardness Hv 62,5	σ_B MPa	Elongation (%)
Treatment in H_2					
800	rapid	17,089	302	941±10	19,2±2,1
	slow	17,091	305	966±12	21,7±0,4
	no treatment	17,088	299	956±5	22,3±1,2
1000	rapid	17,075	306	936±13	14,4±2,2
	slow	17,083	300	955±10	20,4±1,2
	no treatment	17,089	308	953±4	21.0±1,6
1200	rapid	17,067	298	874±38	7,8±1,7
	slow	17,085	305	949±18	21,4±1,3
	no treatment	17,081	303	962±12	21,0±0,8
Treatment in N_2					
800	rapid	17,085	295	947±13	19,6±2,2
	slow	17,084	298	948±18	20,8±1,7
	no treatment	17,093	300	963±10	22.2±0,8
1000	rapid	17,076	310	972±7	19,2±1,8
	slow	17,087	307	970±7	20,8±1,8
	no treatment	17,089	303	967±11	22,8±1,4
1200	rapid	17,079	308	980±8	19,7±2,9
	slow	17,089	304	966±18	22,7±1,7
	no treatment	17,091	309	967±14	22,4±2,2

As shown in the table, in the case of H_2 treatment no
improvements over the as-sintered samples were achieved.
By cooling in the furnace, roughly the same properties
were obtained. Rapid cooling worsened the properties more,
the higher the temperature of the heat treatment was; this
effect agrees well with the observation of Minakova et al.

The heat treatment in N_2 did not improve the properties,
either. There was a marked difference, however, as compared
withthe treatment in H_2: after heat treatment in N_2 the
cooling rate had hardly any effect to the mechanical
properties of the samples. This observation confirms the
theory that H_2 can indeed embrittle W heavy metals, but
only if the samples are cooled too rapidly to enable the
H_2 dissolved in the alloy to escape. At slow cooling rates,
the concentration of hydrogen in the heavy metals falls off
according to the equilibrium and below $800^{\circ}C$ it reaches
harmless values.

If this theory is correct, vacuum treatments should not
improve the properties of heavy metals cooled slowly after
sintering and, as observed with N_2 treatments, the cooling
rate would not have any effect either.

To check this, standard samples were sintered as shown
in fig.21, then they were heat treated at various temperatures
in an induction furnace at 10^{-4} mmHg for 30 min. Together
with the properties of the heat treated samples, those of
as-sintered samples from the same batch are shown.

As expected, no effect of the vacuum heat treatment could
be observed; the values of heat treated and as-sintered
samples were almost identical. Even the elongation, which
is very sensitive to all changes in the production cycle,
was not influenced. This would indicate that vacuum treatments
are not necessary to obtain good elongations if the cooling
after sintering has been slow enough to permit removal all
excess hydrogen from the heavy metals.

Table 8: Properties of samples sintered in Fig.21 and
then vacuum treated as compared to untreated
samples. Sintered 30 min at 1470°C, heat treated
for 30 min. (Average values from 4 samples)

Temp.of heat treatment $^{\circ}$C	Cooling	Density g/cm^3	Hardness Hv 62,5	MPa	Elongation (%)
1000	rapid	17,091	308	952±6	22,7±1,2
	slow	17,083	309	945±2	21,5±1,5
no treatment		17,081	307	952±11	22,2±1,6
1200	rapid	17,089	308	976±10	23,4±0,8
	slow	17,096	306	998±3	24,0±1,0
no treatment		17,094	311	981±8	25,0±0,7

4. Influence of impurities on the mechanical properties

4.1 Metal additives to the binder

As mentioned in the introduction, numerous experiments
have been described in the literature for improving the
properties of heavy metals by adding other metals to the
binder - first with W-Ni-Cu heavy metals (6), then, after
the replacement of Cu by Fe (7), also in the then new
W-Ni-Fe-metals (8). Addition of 30% Co to the binder has
been found advantageous (9), Cr increases the hardness,
but lowers the ductility considerably (10). Since most of
these additives were in the range of several wt%, it was
hoped that a marked decrease in the amount of additives
would either given positive effects on some properties
but suppress negative effects on others, or would largely
retain the positive effect and simply make it possible

to save rare and expensive metals. To that end, 0,5
and 0,05 wt% of six metals were added to the W-Ni-Fe
mixture: Cr, Mo, Co, V and Cu, which had been used
already in earlier experiments (see First Annual Rep.)
and Mn. Cr was added as ferro chromium (12,5 wt% Cr),
all other metals as pure powders. All were sieved to
remove grains >50 um. The preparation of the samples
was carried out in the usual manner; the powders were
mixed in Cyclohexane with 1% Camphor for 3 hrs,
granulated and then pressed with 5,15 ton/cm^2. The green
samples were sintered at 1470°C for different lengths
of time to reveal any accelerating effects of the
additives or the sintering process.

To ensure reliability and reproducibility of the experiments,
in every sintering boat 6 samples with additives, 2 of each
powder charge and 2 standard composition samples were
sintered, arranged as in Fig.26. As our tests had shown,
4 parallel samples are sufficient to give reliable mean
values.
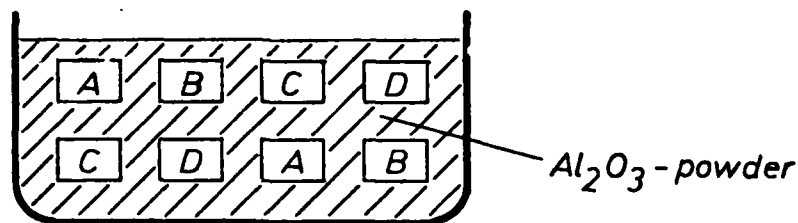
Fig.26: Arrangement of the bars in the sintering
boat

Table 9: Mechanical properties of heavy metals with metal
additives to the binder. 90% W,   Ni:Fe=2:1;
sintered as in Fig.21 at 1470°C (Average values
from 4 samples).

Additive	Sintering time(min)	Density g/cm^3	Hardness Hv 62,5	$\sigma_{\widetilde{o}}$ MPa	Elongation (%)
0,5% Cr	15	17,050	312	977±15	18,1±2,1
	30	17,108	308	921±9	13,9±2,9
	60	17,117	303	853±13	9,9±1,8
0,5% Mo	15	17,123	311	966±16	18,7±0,6
	30	17,128	310	950±23	23,3±1,7
	60	17,113	304	921±11	20,5±1,8
0,5% Co	15	17,117	305	938±8	24,1±0.6
	30	17,115	300	958±6	24,2±0,9
	60	17,117	298	922±14	24,2±1,2
0,5% Cu	15	17,107	298	947±4	14,8±1,0
	30	17,113	292	902±12	12,3±1,7
	60	17,103	296	895±17	11,3±2,3
0,5% V	15	14,341	297	708±24	1,9±0,4
	30	14,714	306	735±18	5,7±2,8
	60	15,218	299	774±31	7,0±1,9
0,5% Mn	15	17,075	302	919±10	11,3±0,5
	30	17,081	311	869±5	10,9±1,0
	60	17,083	308	849±9	11,3±0,8

Table 9: (continued)

Additive	Sintering time(min)	Density g/cm³	Hardness Hv 62,5	σ_{β} MPa	Elongation (%)
0,05% Cr	15	17,103	308	991±5	22,3±2,1
	30	17,099	313	922±11	20,9±0,7
	60	17,081	311	937±7	14,2±0,5
0,05% Mo	15	17,114	311	983±8	22,0±2,0
	30	17,098	314	953±17	23,6±1,5
	60	17,099	308	918±13	20,5±1,8
0,05% Co	15	17,091	307	974±8	21,2±0,8
	30	17,084	311	921±7	20,3±1,7
	60	17,089	311	938±17	11,3±1,6
0,05% Cu	15	17,084	308	956±5	22,2±1,9
	30	17,097	314	949±16	19,3±1,7
	60	17,032	310	922±16	10,6±1,1
0,05% V	15	16,143	297	742±32	2,1±1,1
	30	16,110	292	738±24	5,9±1,8
	60	16,471	301	913±19	8,0±2,7
0,05% Mn	15	17,084	305	976±4	23,6±1,6
	30	17,097	310	956±9	17,3±1,1
	60	17,103	314	958±8	16,4±1,9

The samples containing V showed large swellings both with
0,5 and 0,05% V; pore channels seemed to run through all
the test bars. Apparently a chemical compound forms which
begins to evaporate at sintering temperature; because
of the liquid phase the vapor can not escape from the
bar but forms pores inside the samples. Understandably
the mechanical properties of these samples were very
poor and the tensile strength values were very widely
scattered as compared to the other series.

Addition of 0,5% of other metals did not improve the
properties of the heavy metals as compared to the standard
W-Ni-Fe alloys. Only Co improved the ductility somewhat an
effect observed earlier with higher Co contents (9).

The lower percentage of additives, 0,05% resulted in the
same values as achieved with standard composition, but
only at the rather short sintering time of 15 min. At
longer sintering times the elongation was reduced by Cu
and surprisingly by Co by more than 50%. The embrittlement
caused by 0,5% Cr and Mn was considerably reduced here;
at 15 min. sintering time properties equal to the standard
were measured. In no case could any improvement be realized.

Except for the samples containing V, the reproducibility
was hardly affected by the metal additives and was quite
comparable to that of heavy metals with Ni-Fe binder.

Metallographic investigations:

From metallographic samples etched with $CuSo_4/NH_3$ solution,
average grain sizes were determined by counting the grains
on 0,6 mm long strips and calculating the grain size
after taking into account the area due to binder. From
each sample 9 strips were measured. With this test length,
a surprisingly good rate of reproducibility was achieved.
Tab.10 shows the average grain sizes thus obtained.

Tab.10: Average grain sizes of heavy metals with metal
additives to the binder at different sintering times
(in um)

0,5% additive	15 min	30 min	60 min
Cr	16,1	18,0	22,0
Mo	16,7	19,5	22,3
Co	19,4	20,3	23,6
Cu	18,5	21,4	24,2
V	19,8	21,5	23,6
Mn	18,2	21,5	22,5
(Standard)	18,7	20,7	23,1
0,05% additive			
Cr	18,3	20,2	22,6
Mo	18,9	21,2	23,7
Co	19,4	21,4	24,2
Cu	19,7	20,9	23,8
V	20,0	22,1	24,4
Mn	18,1	20,5	23,7
(Standard)	19,2	21,3	24,0

It seems that Cr and Mo inhibit grain growth, while V
and to a lesser extent, Co, promote it . A definite
connection between grain size and mechanical properties
could not be derived; only the decline of ductility with
grain coarsening was confirmed.

Summarizing, it can be stated that within the elements
and concentration range examined   small amounts of the
investigated metals do not result in significant
improvements in W heavy metal properties. In most cases
deterioration of the mechanical properties was observed.
Such positive effects as that of e.g. Cr on the
ductility of heavy metals, as mentioned in the First
Annual Report apparently are due only to its de-
oxidizing ability. Thorough de-oxidation renders it
useless and sometimes even harmful.

4.2 Heavy metals sintered from W powers doped
with trace impurities

In accordance with our request, 14 special W powders
were produced to be compared to the standard powder W503/79.
Most of these powders contained small amounts of special
impurities which represented those contaminations most
likely to be present in commercial W powders. The powder
E3OW was prepared from impure blue oxide and E33 was not
doped at all for an estimation of the differences between
various undoped powders.

The production of the green compacts was carried out as
described above. The powders were compacted with a pressure
of 5,15 ton/cm^2. No difficulties, such as pressing faults,
were encountered, except with powder E8W, which at first
resulted in horizontal cracks. A second granulation of
the green compacts and subsequent pressing resulted in
faultless samples. These difficulties probably had been
caused by the unsatisfactory flow behavior of the powder;
instead of flowing uniformly, the powder mixture formed
lumps which caused inhomogeneous filling of the die and
in due course tensions in the green compacts which
caused them to crack. This tendency to form lumps had
been observed earlier and was the source of trouble
with fine powders (see First Annual Report).

For the sintering of the samples, the sintering cycle
found to be optimal in earlier investigations was selected
(First Annual Report, Sintering Cycle Fig.2). The
temperature-time diagram is shown in Fig.21. After a
60 min de-waxing treatment at 500°C, thorough pre-
reduction ensured complete removal of oxygen. For that
purpose the furnace was heated in 6 hrs from 500 to
1400°C. At that temperature, the Mo boats containing
the samples was pulled into a somewhat cooler section
of the furnace and was then pushed back into the heating
zone when the furnace had reached sintering temperature.
The sintering time could thus be determined very exactly.
After sintering, the furnace was simply switched off.
It cooled down to 500°C in 14 hrs at which temperature
the boat was pulled stepwise out of the furnace.

To enable a meaningful comparison between the samples
prepared from doped W powders and those prepared from
standard W503/79, 4 doped samples and 4 standard bars,
arranged in a checker board pattern to compensate for
all possible differences in temperature distribution
during the sintering process, were sintered in every batch
(Fig.27). To give reliable average results, at least
10 samples were prepared and tested from each powder.
This was necessary because the difference, especially
for the elongations, between standard and doped samples
was sometimes hardly detectable.
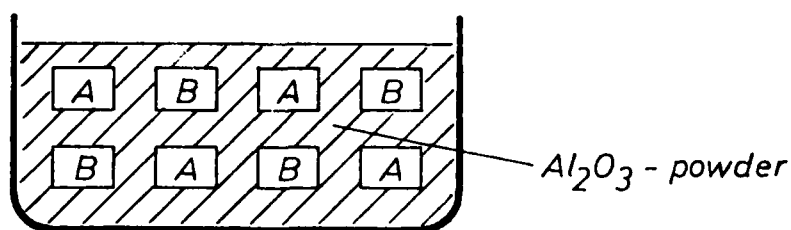
Fig.27: Arrangement of the bars in the sintering
boat

To further illustrate the scatter in the values for
tensile strength and elongation, the results were
evaluated using Weibull-statistics (11). From a certain
number of values, the probability of fracture at a given
stress can be derived. On the other hand, it is possible
to determine the stress which would cause 50% of the
samples to break.

The probability of fracture (P) is influenced by the
sample volume (V) , tensile strength (σ) and a parameter
indicating the homogeneity of the material (m), following
the equation

$$P = 1 - 1/\exp. \frac{V}{V_o} \cdot (\frac{\sigma}{\sigma_0})^m \qquad (V_o, \sigma_o \text{ refer to standard sample})$$

The equation is then transformed and σ_{50} inserted

$$\lg\lg \frac{1}{1-P} - \lg\lg 2 = m \cdot (\lg\sigma - \lg \sigma_{50})$$

For a given amount N of samples, the P values depend only
on the sample number n (from 1 to N). The graphic evaluation
is carried out by taking the left side of the equation for
the x-values and the right for y-values.

$$x = \lg\lg \frac{1}{1-P} \quad \text{and with} \quad P_n = \frac{n}{N+1}$$

$$x = \lg\lg \frac{N+1}{N+1-n}$$

$$y = \lg \sigma$$
$$s_w = 1/m$$

This is the equation of a straight line

$$y - y_{50} = s_w \cdot (x - x_{50})$$

The slope of the Weibull straight line indicates
the scatter of the individual values; the broader
the scatter, the more pronounced the slope and the
greater the probability of fractures occurring below
the average tensile strength.These statistics take into
account the imperfections in the individual samples
which are the main initiators of fracture. The probability
of fracture at a given stress is determined by number,
distribution and kind of imperfections. The Weibull
statistics have been used successfully in many cases and
for a given purpose are usually more reliable than the
usual Gaussian distribution. In the following tables the
arithmetic means and standard deviations for all properties
are shown after the individual values. For each charge
with values from doped and standard samples the Weibull-
diagrams for tensile strength and elongation are also
given.

Powder E2 (250 ppm Na)

Table 11: Mechanical properties of the samples prepared
from E2 and of the comparison samples from 5o3

ST	TP	E 2				5o3			
°C	°C	ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
147o	2 +	17,1o63	962	24,o	3o7	17,o931	943	21,4	292
		17,o971	955	22,6	299	17,1o6o	955	22,o	292
		17,1o84	964	23,o	3o5	17,o887	948	2o,o	294
		17,o962	946	2o,4	291	17,o899	943	18,8	298
1475	3 +	17,1o44	943	23,6	3o3	17,o941	936	2o,2	299
		17,o826	944	21,6	3o4	17,o988	962	23,6	296
		17,o751	95o	25,2	293	17,o866	962	26,2	293
		17,o9o5	948	21,6	3o4	17,o815	964	19,2	298
1475	3 +	17,o759	945	22,6	3o1	17,o8o3	96o	22,8	296
		17,o936	973	21,4	3o6	17,o854	948	2o,6	296

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_{5o} MPa	s_σ $.10^{-2}$	δ_{5o} %	s_δ $.10^{-2}$
E 2	12,o2 ± o,o1	17,o9 ± o,o1	29,7	3o2 ± 5	954	o,947	22,7	6,o57
5o3	11,7o ± o,o2	17,o9 ± o,o1	31,5	295 ± 3	953	1,oo2	21,6	9,56o

ST .. Sintering temperature
TP .. Dew point
ρ_{Gr} .. density of green sample
ρ .. density of sintered sample

SS .. Shrinkage during sintering
s_σ, s_δ .. slope values of the Weibull straight lines

Fig.28: Weibull-Diagrams for powder E2
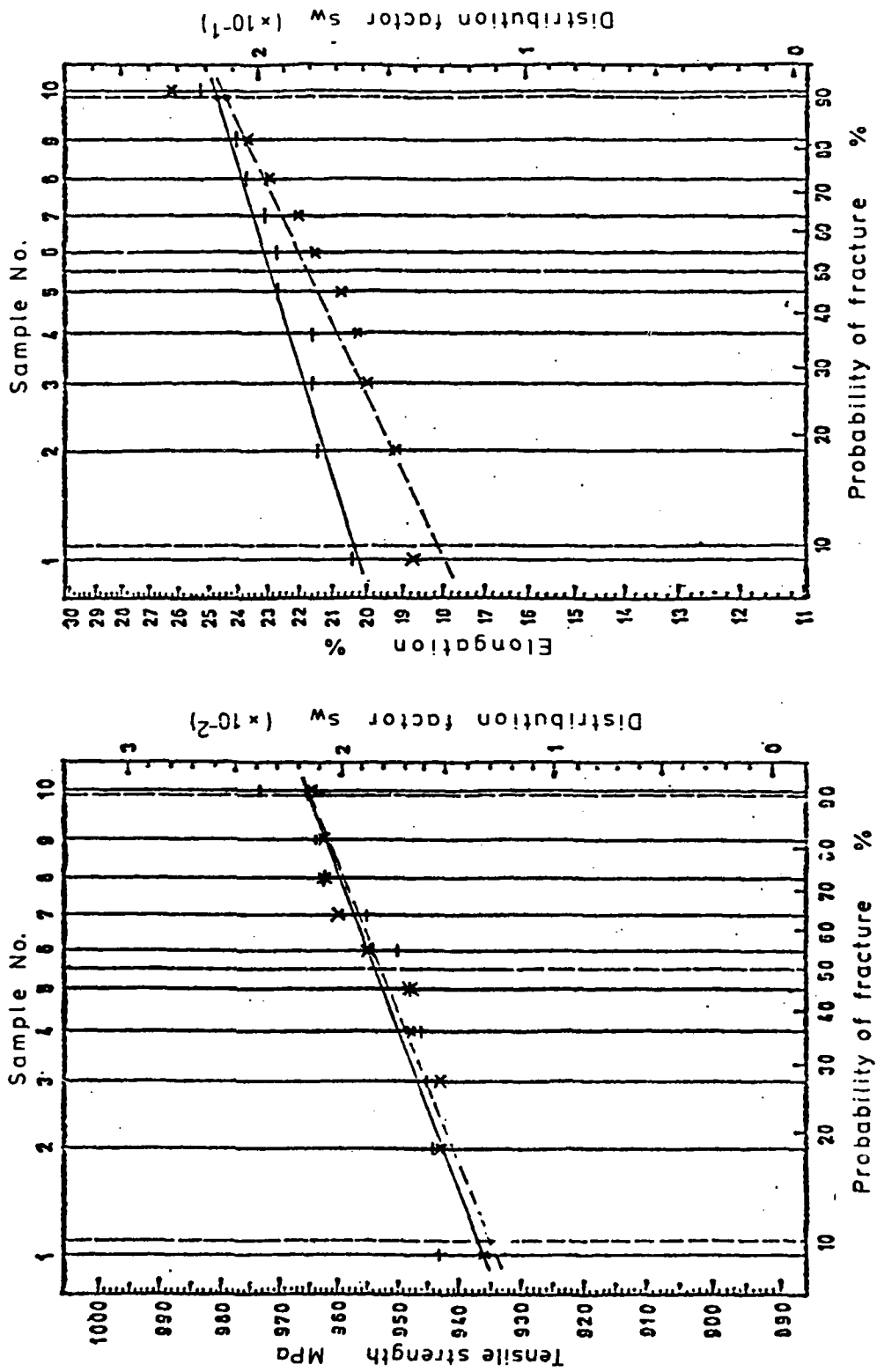
solid line and – for powder E2

broken line and x for standard powder W503

Powder E5 (250 ppm Li)

Table 12: Mechanical properties of the samples prepared from E5 and of the comparison samples from 503

ST °C	TP °C	ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
						E 5 → 503			
1470	5 +	17,0914	934	18,0	290	17,0837	948	22,8	296
		17,0938	939	18,4	292	17,0736	945	20,0	302
		17,1023	945	21,4	297	17,1034	958	20,0	299
		17,1068	958	19,4	292	17,0844	951	20,0	298
1480	4 +	17,1042	934	17,6	297	17,0899	942	20,8	295
		17,1068	941	18,8	297	17,0958	938	20,0	293
		17,1058	955	22,0	301	17,0957	949	24,0	301
		17,0940	964	23,4	302	17,0935	962	24,4	298
1480	5 +	17,0788	936	17,6	296	17,0866	962	26,2	293
		17,0853	952	21,1	291	17,0803	960	22,8	296

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_{50} MPa	s_σ .10^{-2}	δ_{50} %	s_δ .10^{-2}
E 5	12,31 ± 0,02	17,10 ± 0,01	28,0	295 ± 4	947	1,063	19,9	9,523
503	11,70 ± 0,01	17,09 ± 0,01	31,5	297 ± 3	953	0,898	22,3	9,008

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Fig.29: Weibull-Diagrams for powder E5

solid line and   —   for powder E5

broken line and   x   for standard powder W503

Powder E8 (188 ppm Ca)

Table 13: Mechanical properties of the samples prepared from E8 and of the comparison samples from 5o3

ST °C	TP °C	E 8 ρ g/cm³	$\widetilde{\sigma}_B$ MPa	δ %	H_V	5o3 ρ g/cm³	$\widetilde{\sigma}_B$ MPa	δ %	H_V
147o	3+	17,o556	981	22,4	294	17,o855	968	2o,8	298
		17,o657	946	22,4	292	17,o75o	955	2o,o	295
		17,o627	974	22,o	294	17,o923	966	23,o	297
		17,o722	976	23,2	299	17,o955	969	21,2	294
1475	3+	17,o34o	956	21,2	299	17,o762	966	2o,8	297
		17,o523	966	23,o	294	17,o611	973	22,o	299
		17,o614	956	22,4	3o2	17,o454	975	22,4	292
		17,o437	974	24,8	299	17,o681	97o	2o,4	292
148o	5+	17,o251	971	24,8	3oo	17,o866	962	26,2	296
		17,o311	969	23,6	297	17,o8o3	96o	22,8	293

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	$\widetilde{\sigma}_{5o}$ MPa	s_σ .1o^{-2}	δ_{5o} %	s_δ .1o^{-2}
E 8	11,73 ± o,o2	17,o5 ± o,o2	31,2	297 ± 3	968	1,115	23,1	4,773
5o3	11,7o ± o,o2	17,o8 ± o,o1	31,5	295 ± 2	967	o,6o2	22,1	7,o45

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Fig.30: Weibull-Diagrams for powder E8

solid line and — for powder E8

broken line and x for standard powder W503

Powder E11 (250 ppm B)

Table 14: Mechanical properties of the samples prepared
from E11 and of the comparison samples from 5o3

ST TP		E 11				5o3			
^{o}C ^{o}C		ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
147o 3 +		17,o652	995	25,4	291	17,o727	964	2o,o	292
		17,o711	977	22,6	289	17,o577	966	2o,o	297
		17,o776	979	22,o	289	17,o574	963	2o,2	292
		17,o638	97o	21,o	29o	17,o6o6	978	2o,o	299
148o 2 +		17,o781	984	2o,8	291	17,o623	969	21,8	287
		17,o648	973	23,4	29o	17,o6oo	961	21,2	295
		17,o765	968	2o,o	291	17,o618	974	25,o	292
		17,o9o5	976	22,2	9oo	17,o655	98o	2o,8	295
1475 5 +		17,o634	945	2o,8	3o2	17,o7o8	965	25,2	295
		17,o671	965	23,6	298	17,o798	96o	2o,2	297

Mean values ± standard deviations

	ρ_{Gl} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{5o} MPa	s_σ .1o^{-2}	δ_{5o} %	s_δ .1o^{-2}
E 11	1o,94 ± o,04	17,o7 ± o,o1	35,9	293 ± 5	976	1,168	22,3	6,863
5o3	11,7o ± o,o1	17,o6 ± o,o1	31,4	294 ± 3	957	o,667	21,5	7,185

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Fig.31: Weibull Diagrams for powder E11

solid line and — for powder E11

broken line and x for standard powder W503

Powder E14 (250 ppm Al)

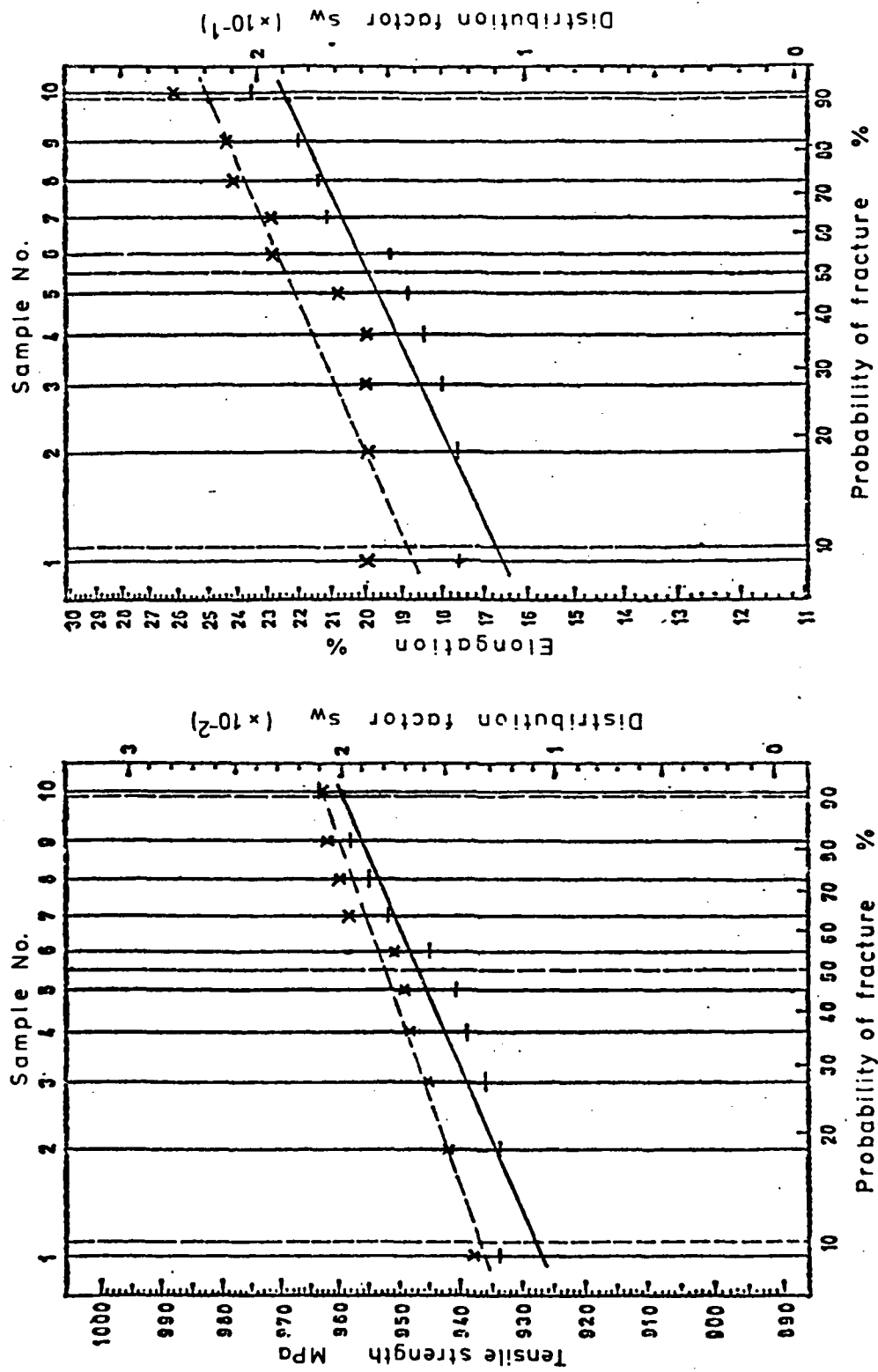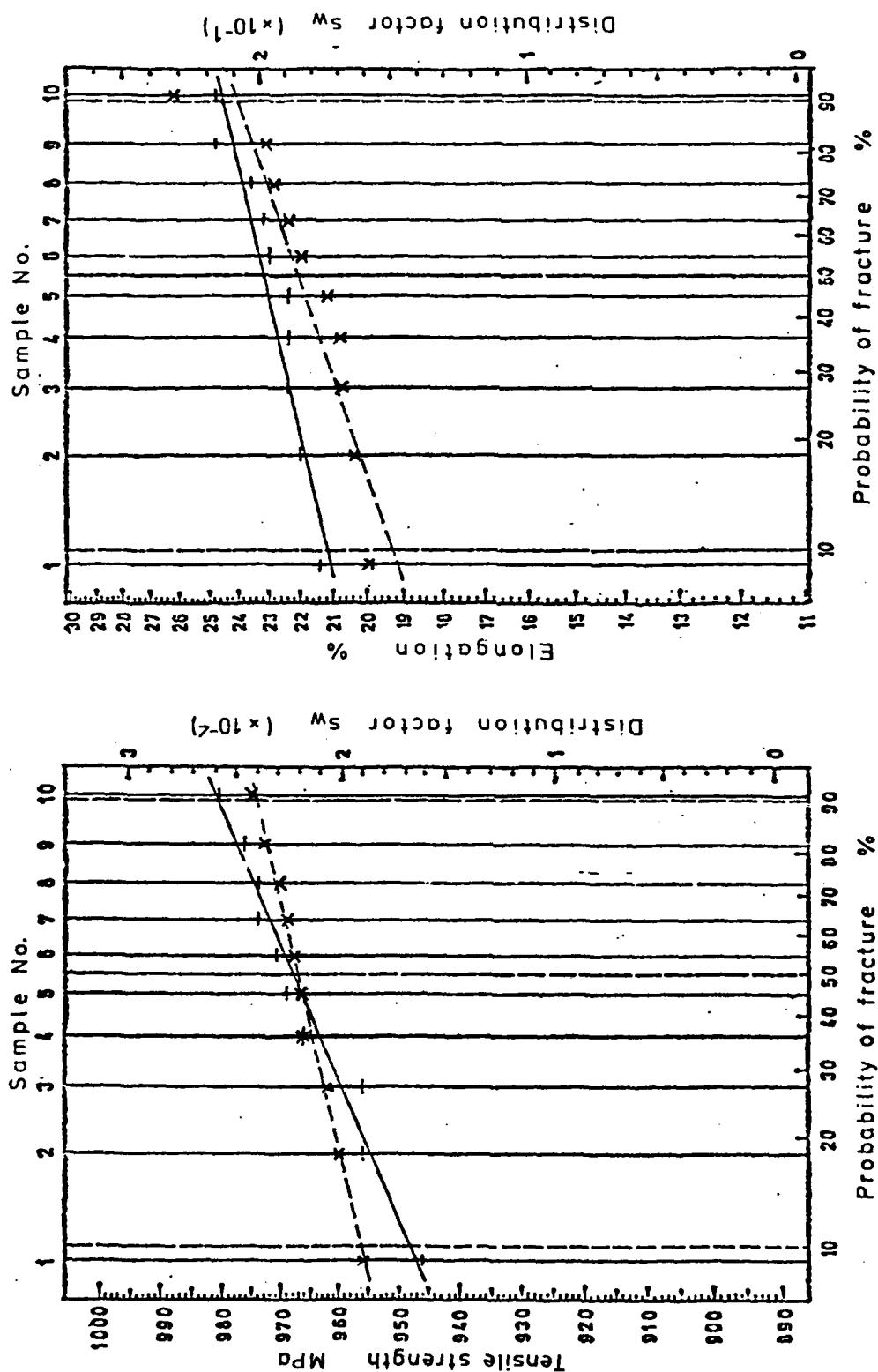Table 15: Mechanical properties of the samples prepared
from E14 and of the comparison samples from 503

ST TP °C °C	E 14 ρ g/cm³	σ_R MPa	δ %	H.	50. ρ g/cm³	σ MPa	δ %	H_v
1475 +2	17,0333	953	15,2	292	17,0708	974	22,6	297
	17,0402	960	18,4	295	17,0736	963	18,4	299
	17,0359	957	18,0	297	17,0862	981	23,2	293
	17,0494	953	19,6	295	17,0802	966	24,0	295
1475 +3	17,0387	897	10,8	292	17,0708	965	25,2	295
	17,0312	950	17,6	300	17,0798	960	20,2	297
	17,0396	881	8,8	290	17,0650	937	19,6	296
	17,0299	925	15,2	290	17,0433	959	20,8	293
1475 +2	17,0478	920	19,6	293	17,0941	951	22,0	297
	17,0491	926	18,4	297	17,0883	938	21,4	296

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_v	$\overline{\sigma}_{50}$ MPa	s_σ .10⁻²	$\overline{\delta}_{50}$ %	s_δ .10⁻²
E 14	11,56 ± 0,01	17,04 ± 0,01	32,2	294 ± 3	935	2,866	16,2	25,368
503	11,70 ± 0,01	17,07 ± 0,01	31,5	296 ± 2	959	1,440	21,7	9.554

Fig.32: Weibull Diagrams for powder E14

solid line and — for powder E14

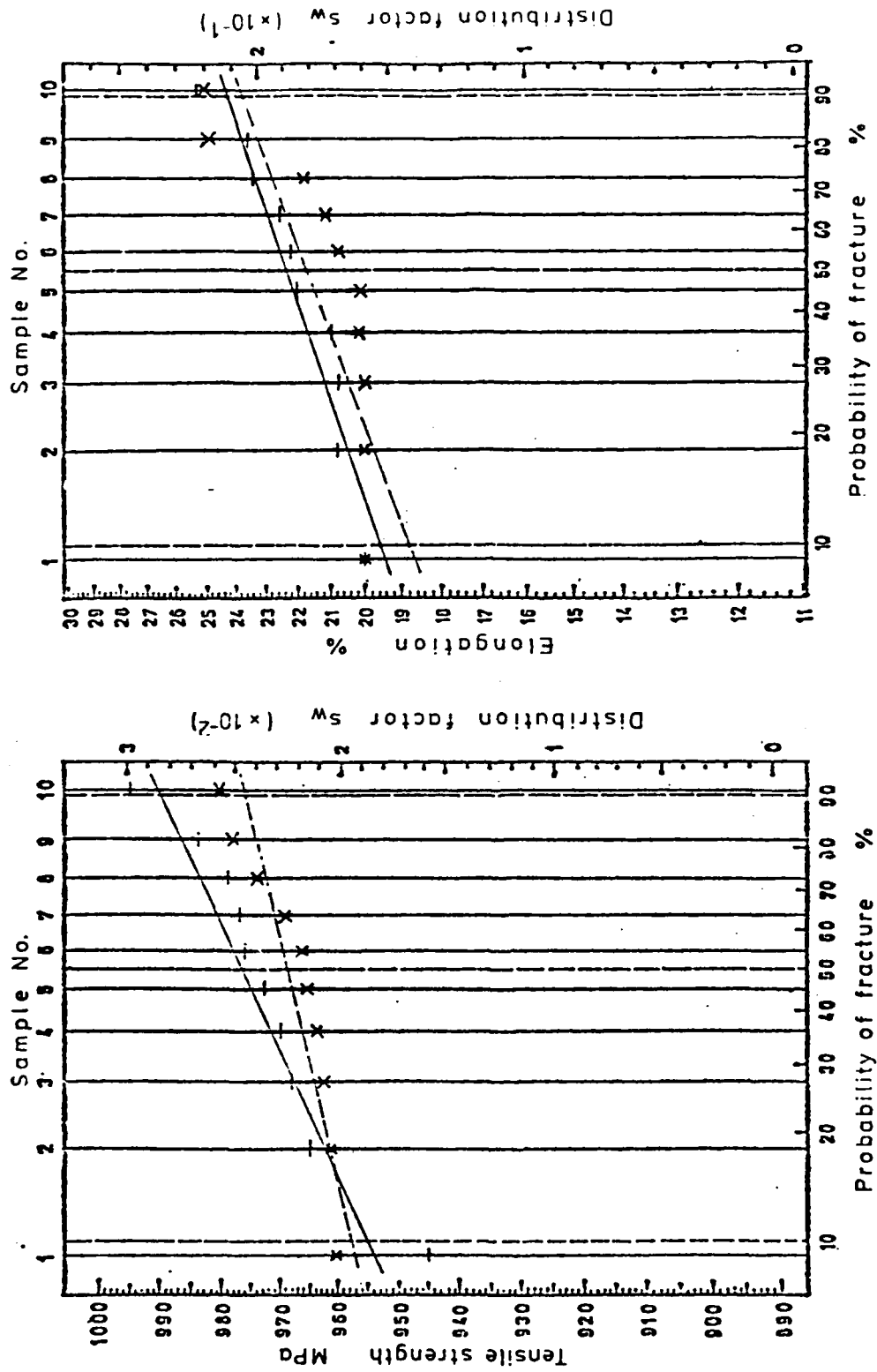broken line and x for standard powder W503

Powder E17 (100 ppm Si)

Table 16: Mechanical properties of the samples prepared
from E17 and of the comparison samples from 5o3

ST TP $^{\circ}$C $^{\circ}$C	E 17				5o3			
	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_D MPa	δ %	H_V
1485 +7	17,o321	924	21,6	297	17,o468	926	24,o	296
	17,o117	928	2o,o	3o2	17,o538	932	23,2	292
	17,o23o	925	24,8	291	17,o514	918	19,8	298
	17,o392	927	26,o	29o	17,o336	917	19,o	293
149o +3	17,o176	924	22,8	3o2	17,o329	916	21,o	296
	17,o444	93o	23,4	291	17,o385	917	25,o	295
148o +3	17,o285	953	23,6	292	17,o659	944	23,2	292
	17,o448	941	25,2	292	17,o676	951	22,o	292
	17,o625	953	23,4	295	17,o6o9	949	23,8	287
	17,o499	935	2o,8	292	17,o5o2	952	22,o	291

Mean values $\pm$ standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{5o} MPa	s_σ .1o^{-2}	δ_{5o} %	s_δ .1o^{-2}
E 17	11,76 $\pm$ o,o1	17,o4 $\pm$ o,o2	31,o	294 $\pm$ 5	935	1,o41	23,o	6,942
5o3	11,7o $\pm$ o,o1	17,o5 $\pm$ o,o1	31,4	293 $\pm$ 3	934	1,5oo	22,5	8,694

Fig.33: Weibull Diagrams for powder E17

solid line and – for powder E17

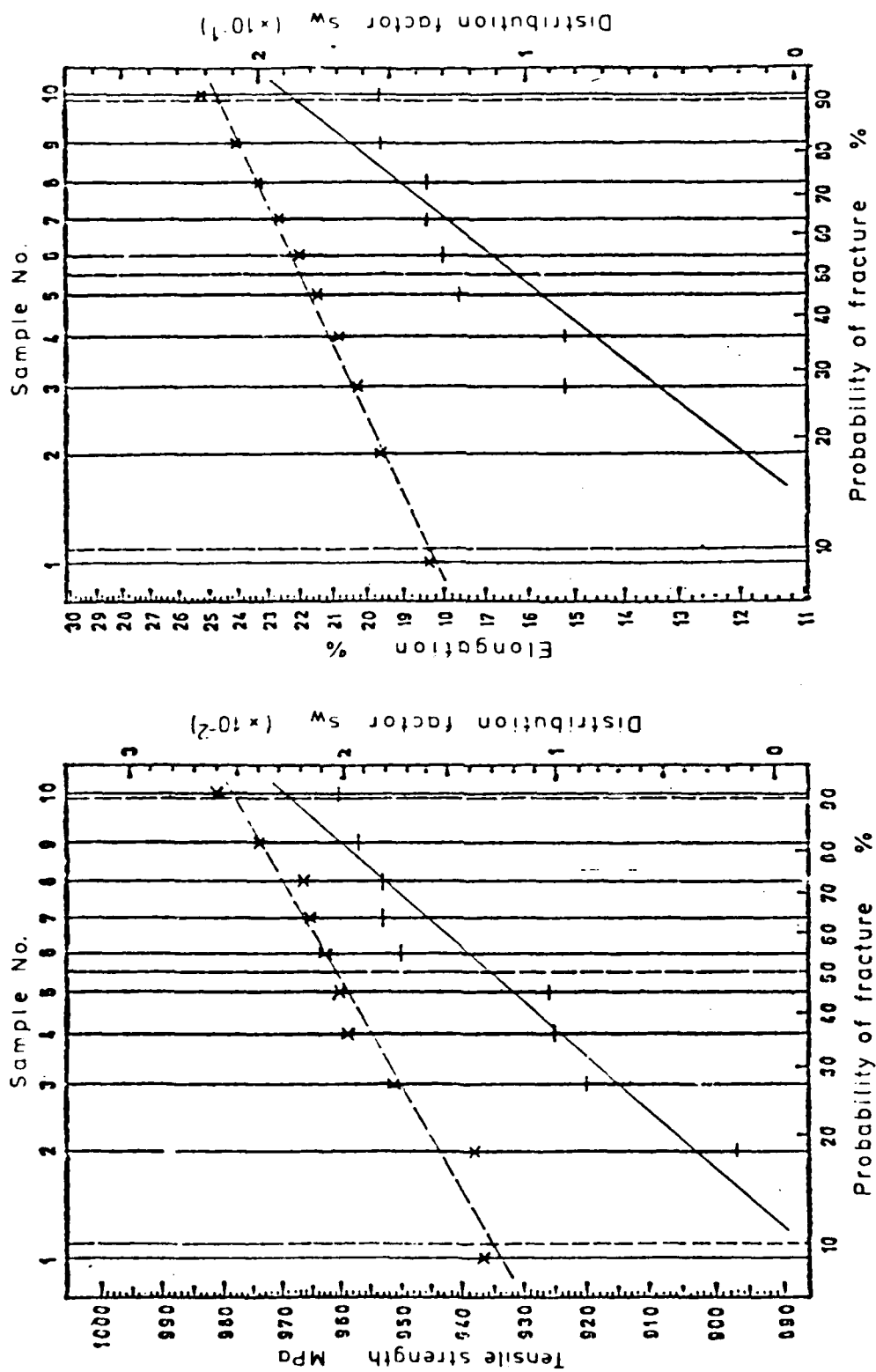broken line and x for standard powder W503

Powder E21 (140 ppm Na, 100 ppm P)

Table 17: Mechanical properties of the samples prepared
from E21 and of the comparison samples from 5o3

ST °C	TP °C	E 21				5o3			
		ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
1485	+ 2	17,o95o	911	21,4	297	17,o942	92o	22,2	29o
		17,o79o	936	22,4	3o2	17,o715	911	26,o	291
		17,o81o	916	25,8	289	17,o749	92o	22,4	297
		17,1o14	937	2o,o	292	17,o7o1	942	24,8	289
1485	+ 2	17,o848	953	21,4	289	17,1oo4	935	21,2	294
		17,o752	926	19,4	289	17,o99o	95o	21,4	297
		17,o785	936	2o,8	292	17,o615	941	2o,o	291
		17,1oo8	922	2o,o	292	17,o38o	927	21,2	292
149o	+ 3	17,o555	916	21,6	289	17,o498	93o	2o,o	295
		17,o713	915	21,o	3oo	17,o385	917	25,o	295

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	$\tilde{\sigma}_{5o}$ MPa	$\hat{s}_\sigma$ .10^{-2}	$\tilde{\delta}_{5o}$ %	s_δ .10^{-2}
E 21	11,8o ± o,o3	17,o8 ± o,o1	3o,9	292 ± 4	928	1,319	21,5	6,769
5o3	11,7o ± o,o1	17,o7 ± o,o2	31,5	293 ± 3	931	1,31o	22,6	8,655

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Fig.34: Weibull Diagrams for powder E21

solid line and — for powder E21

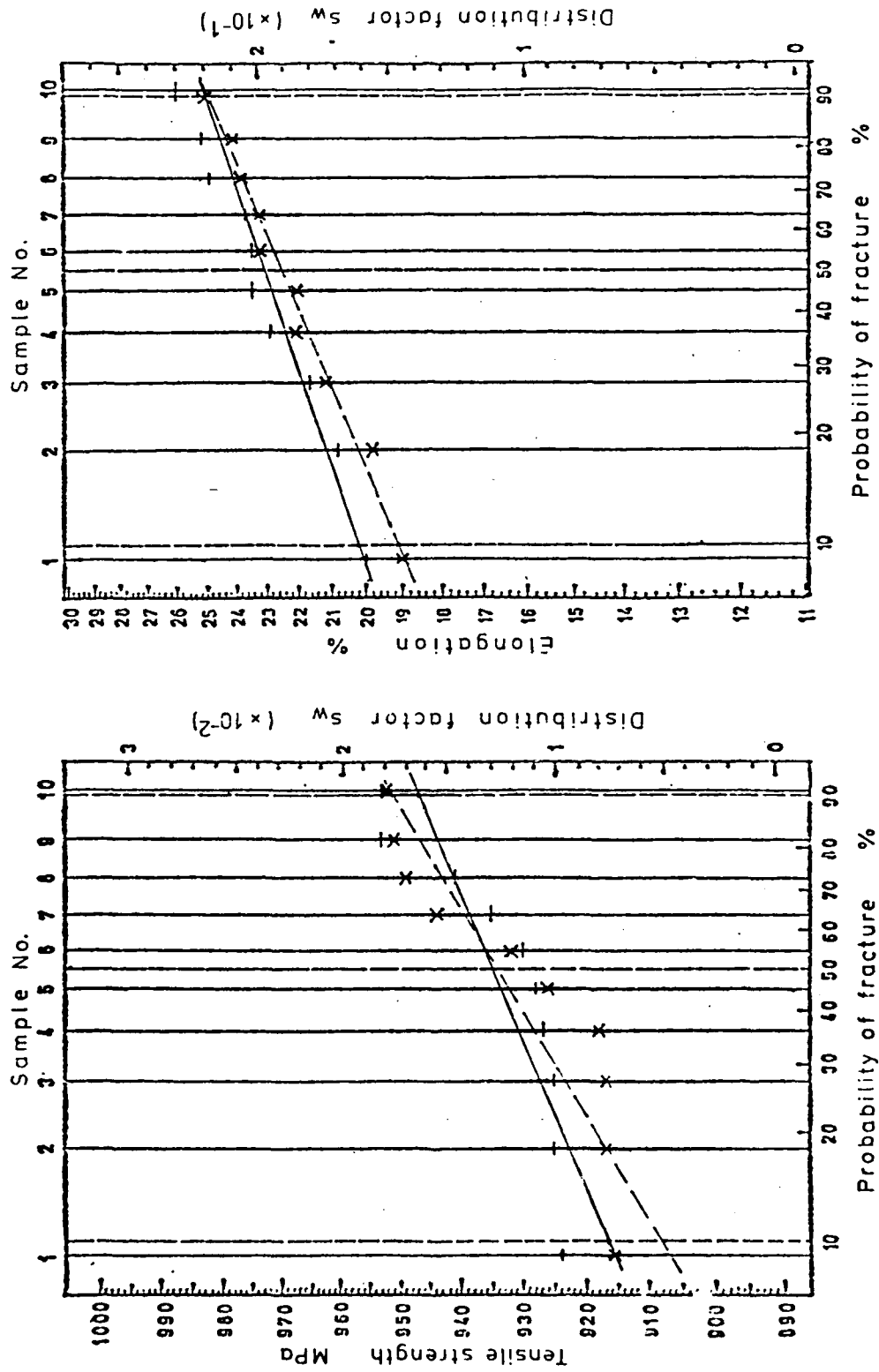broken line and x for standard powder W503

Powder E24 (je 100 ppm As, Sb, Bi)

Table 18: Mechanical properties of the samples prepared
from E24 and of the comparison samples from 503

ST °C	TP °C	E 24				5o3			
		ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
1485	5+	17,o72o	92o	2o,6	297	17,o724	93o	21,6	295
		17,o628	927	21,4	287	17,o569	918	19,2	292
		17,o926	93o	2o,o	29o	17,o7o7	931	21,8	289
		17,o633	924	22,o	29o	17,o764	92o	2o,o	294
1485	3+	17,o491	945	18,4	286	17,o589	929	2o,6	291
		17,o67o	946	2o,2	284	17,o482	931	2o,6	284
		17,o574	95o	21,2	292	17,o812	911	18,4	287
1485	1+	17,o8o5	926	2o,o	293	17,o38o	927	21,2	292
		17,o686	927	2o,6	292	17,o498	93o	2o,o	295
		17,o834	957	2o,4	293	17,o556	927	2o,o	295

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_{5o} MPa	s_σ .10⁻²	δ_{5o} %	s_δ .10⁻²
E 24	11,45 ± o,o1	17,o7 ± o,o1	32,9	29o ± 4	937	1,255	2o,6	4,875
5o3	11,7o ± o,o1	17,o6 ± o,o1	31,4	291 ± 4	926	o,699	2o,5	5,145

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Fig.35: Weibull Diagrams for powder E24

solid line and — for powder E24

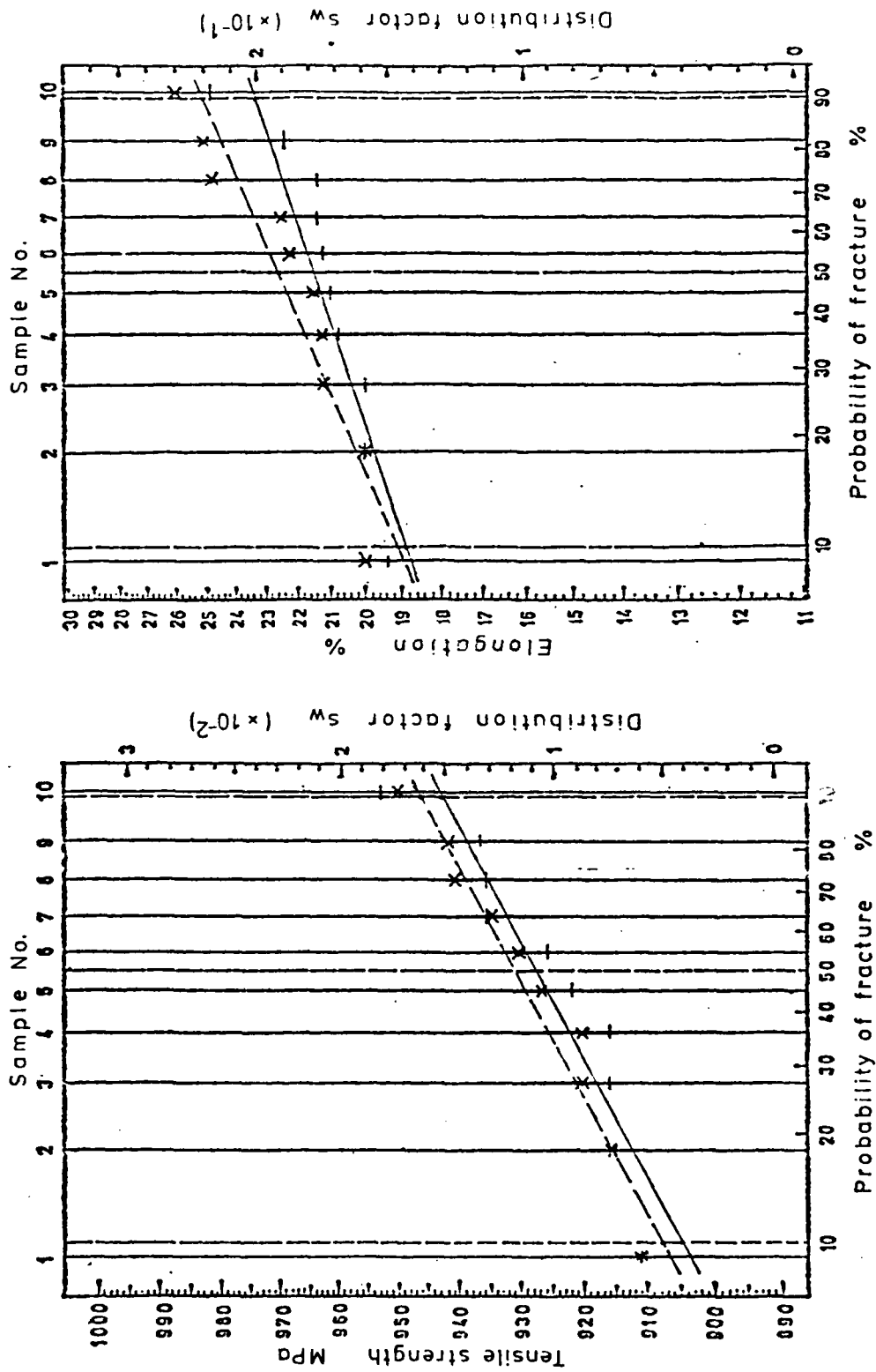broken line and x for standard powder W503

Powder E27 (100 ppm U)

<u>Table 19:</u> Mechanical properties of the samples prepared
from E27 and of the comparison samples from 5o3

ST °C	TP °C	E 27 ρ g/cm^3	σ_B MPa	δ %	H_V	5o3 ρ g/cm^3	σ_B MPa	δ %	H_V
1475	6 +	17,1o1o	925	26,2	3o2	17,0721	9o4	21,2	295
		17,o923	931	26,8	3o2	17,o855	928	24,8	292
		17,o795	946	23,8	292	17,o8o2	94o	2o,8	295
		17,o748	956	23,8	298	17,o949	944	22,8	292
147o	5 +	17,o855	941	23,4	3o2	17,o715	958	18,4	292
		17,o7o2	938	22,4	294	17,o796	958	2o,2	295
147o	3 +	17,o722	926	23,6	295	17,o796	921	2o,2	293
		17,o993	944	21,2	3o1	17,o861	935	2o,4	294
		17,o725	93o	22,8	296	17,o898	938	21,8	294
		17,o745	841	24,8	294	17,o834	938	2o,2	298

Mean values <u>+</u> standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{5o} MPa	s_σ .1o^{-2}	δ_{5o} %	s_δ .1o^{-2}
E 27	11,82 ± o,o4	17,o8 ± o,o1	3o,8	298 ± 4	939	o,998	24,o	6,737
5o3	11,7o ± o,o1	17,o8 ± o,o1	31,5	296 ± 5	938	1,699	21,2	7,412

Distribution factor S_w $(\times 10^{-1})$

Sample No.

Probability of fracture %

Elongation %

Distribution factor S_w $(\times 10^{-2})$

Sample No.

Probability of fracture %

Tensile strength MPa

Fig.36: Weibull Diagrams for powder E27

solid line and – for powder E27
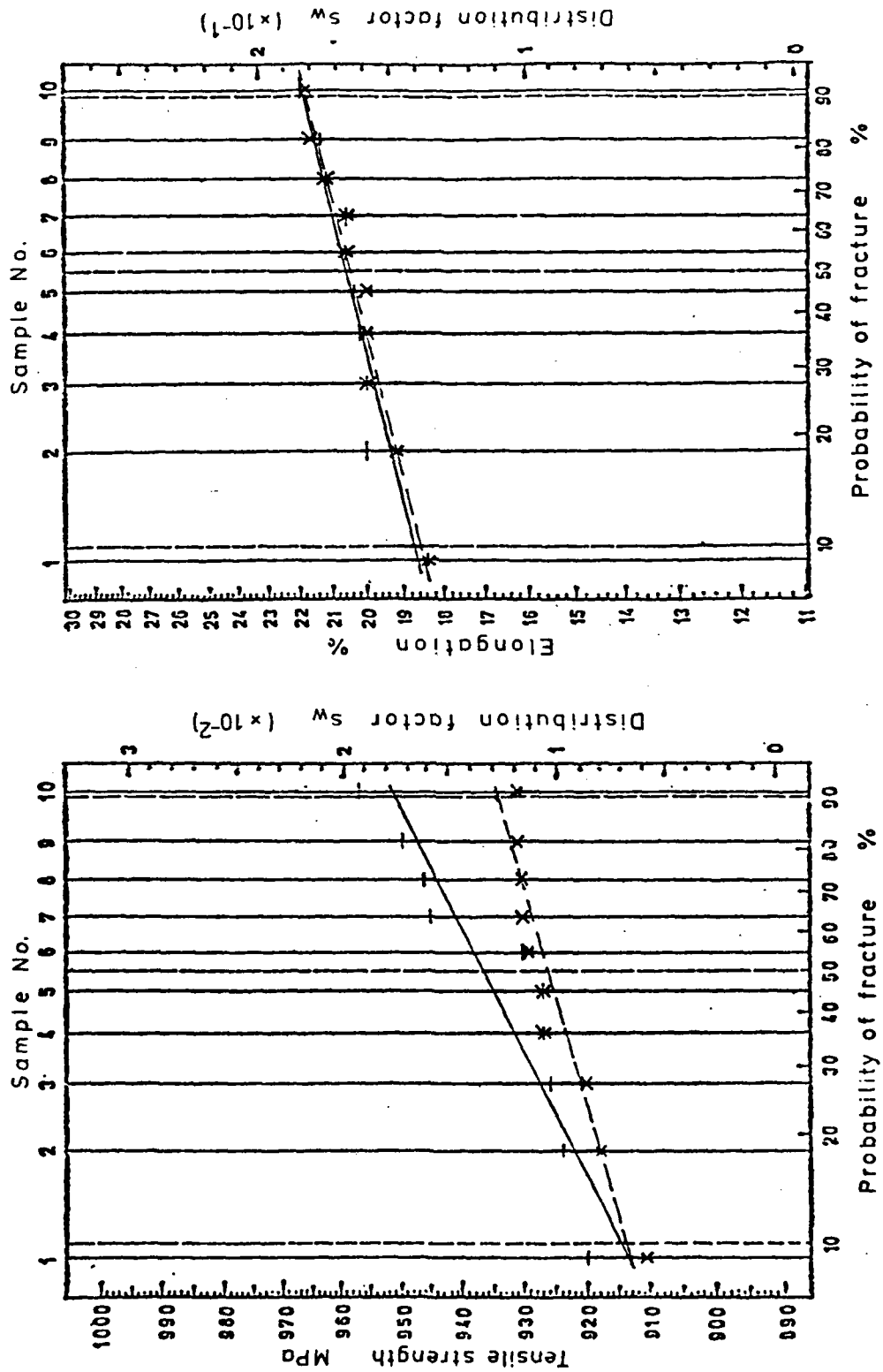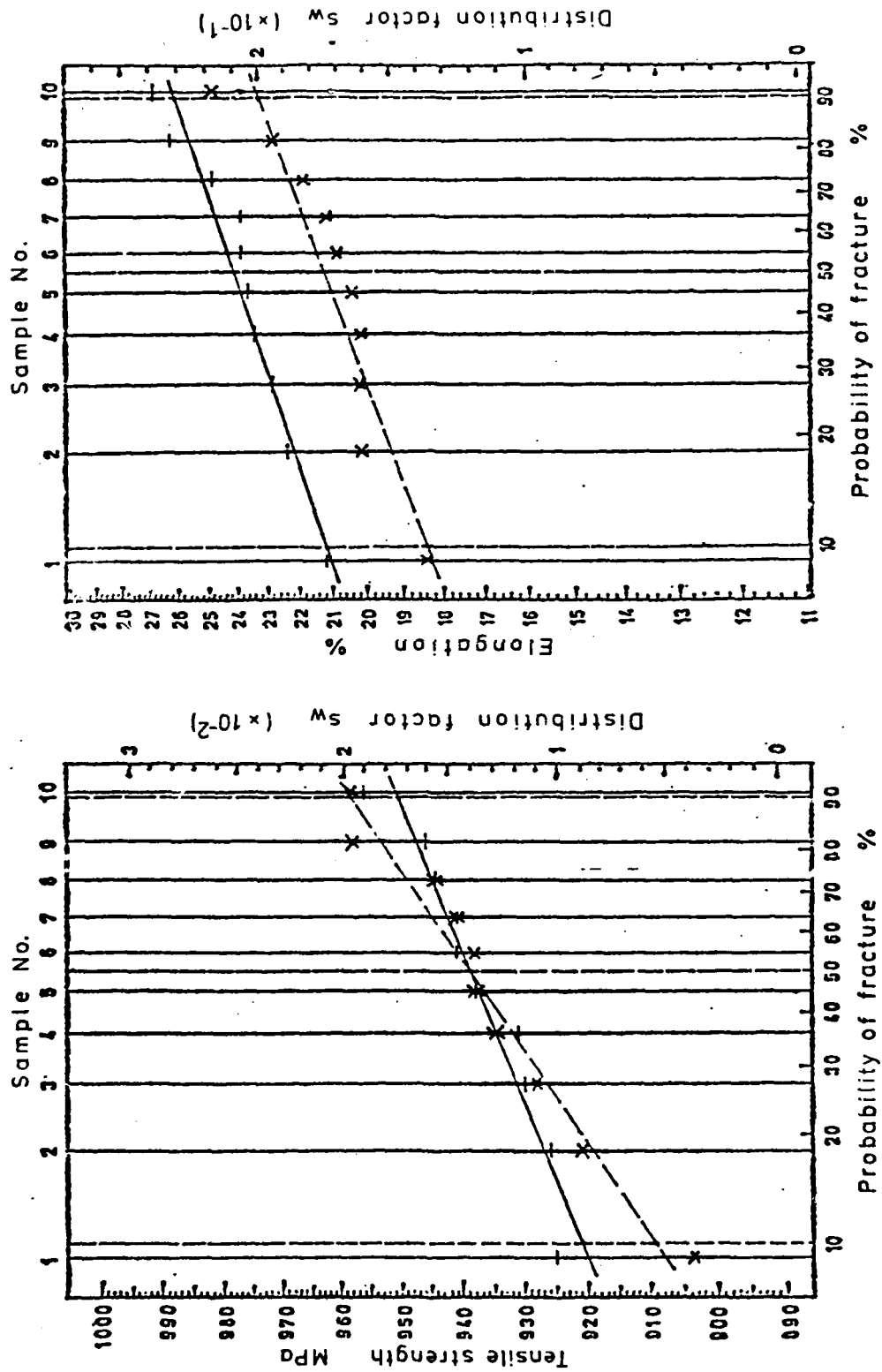broken line and x for standard powder W503

Powder E30 (188 ppm Na, 113 ppm U, 106 ppm Al, 500 ppm F)

Table 20: Mechanical properties of the samples prepared
from E30 and of the comparison samples from 503

ST °C	TP °C	E 3o ρ g/cm³	σ_B MPa	δ %	H_V	5o3 ρ g/cm³	σ_s MPa	δ %	H_V
1480	5 -	17,0374	927	2o,o	3oo	17,0618	941	23,8	297
		17,0488	912	2o,4	295	17,0625	92o	22,4	29o
		17,0428	915	2o,4	295	17,0623	925	23,4	287
		17,0524	924	24,4	298	17,02oo	921	21,6	293
147o	3 +	17,0166	922	2o,4	29o	17,04o4	947	21,6	3o6
		17,0293	916	21,2	293	17,0299	934	21,6	291
149o	o	17,0349	958	22,o	298	17,0491	937	22,6	295
		17,0337	953	21,4	292	17,0533	942	21,4	29o
		17,0292	944	2o,8	298	17,043o	938	22,8	29o
		17,0385	934	2o,6	299	17,05o4	937	24,o	296

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_{5o} MPa	s_σ .1o⁻²	δ_{5o} %	s_δ .1o⁻²
E 3o	11,86 ± o,o1	17,o3 ± o,o1	3o,4	295 ± 3	932	1,61o	21,3	4,661
5o3	11,7o ± o,o1	17,o5 ± o,o1	31,4	29⁴ ± 6	935	o,956	22,6	4,oo1

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Distribution factor s_w $(\times 10^{-1})$

Sample No.

Probability of fracture %

Elongation %

Distribution factor s_w $(\times 10^{-2})$

Sample No.

Probability of fracture %

Tensile strength MPa

Fig. 37: Weibull-Diagrams for powder E30
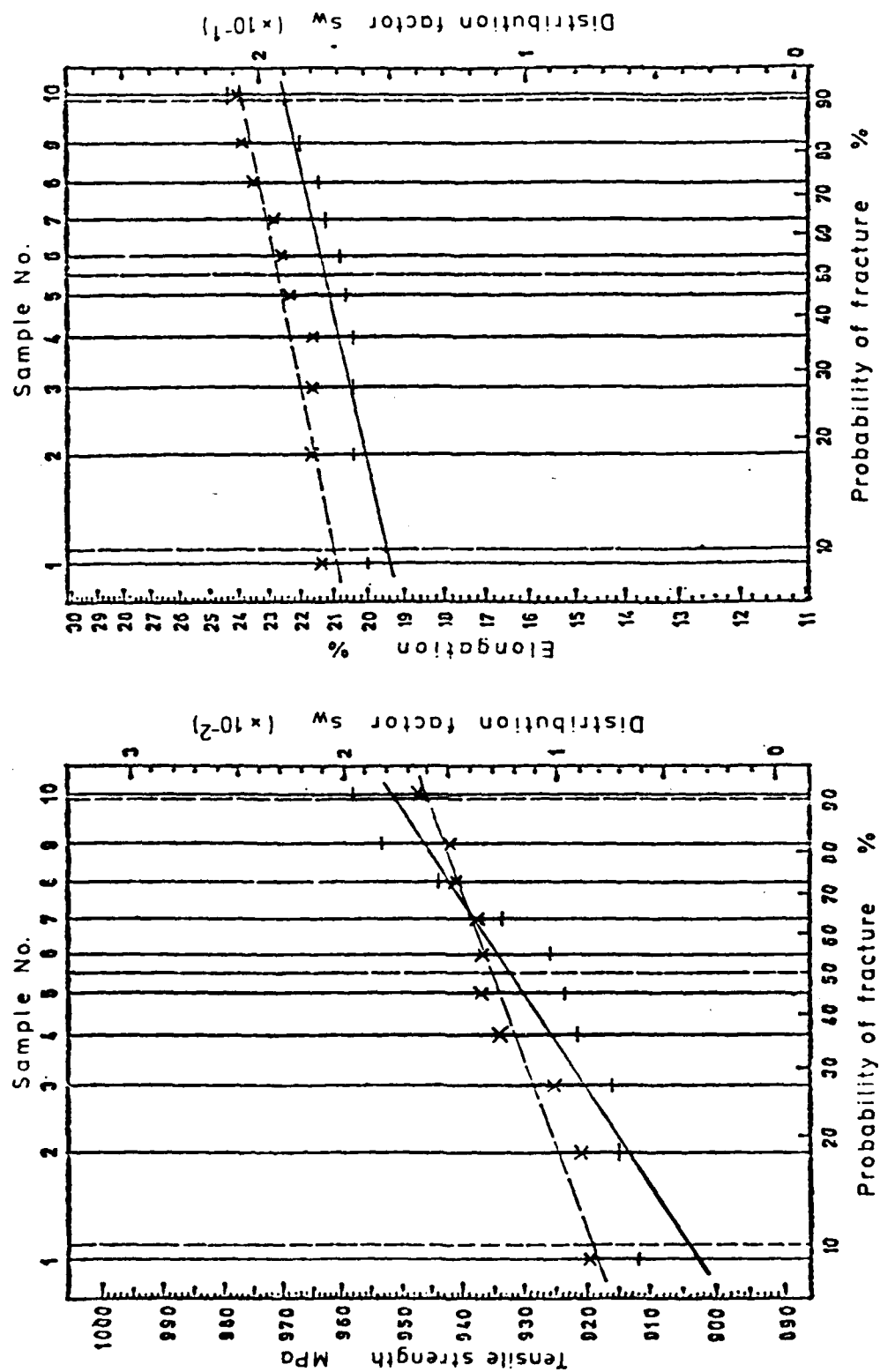
solid line and — for powder E30

broken line and x for standard powder W503

Powder E33   (no doping additives)

Table 21: Mechanical properties of the samples prepared
from E33 and of the comparison samples from 503

ST TP °C °C		E 33				503			
		ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
1470	4 +	17,0799	966	20,4	292	17,0930	983	19,2	291
		17,0637	960	21,6	297	17,0836	976	20,4	292
		17,0769	976	20,8	295	17,0758	981	20,8	291
		17,0765	983	20,0	290	17,0850	969	19,6	296
1480	5 +	17,0688	961	22,0	295	17,0620	956	20,4	293
		17,0483	936	20,0	295	17,0694	955	21,0	296
		17,0599	944	24,6	298	17,0647	961	21,2	291
		17,0643	942	22,0	291	17,0836	953	22,0	296
1475	3 +	17,0708	965	25,2	295	17,0813	969	23,6	297
		17,0798	960	20,2	297	17,0707	959	23,6	293

Mean values $\pm$ standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_{50} MPa	s_{σ} .10^{-2}	δ_{50} %	s_{δ} .10^{-2}
E 33	11,87 ± 0,01	17,07 ± 0,01	30,5	294 ± 3	961	1,508	22,0	6,455
503	11,70 ± 0,01	17,08 ± 0,01	31,5	294 ± 2	966	1,073	21,3	6,547

Distribution factor S_W $(\times 10^{-1})$

Sample No.

Probability of fracture %

Elongation %

Distribution factor S_W $(\times 10^{-2})$

Sample No.

Probability of fracture %

Tensile strength MPa

Fig. 38: Weibull Diagrams for powder E33

solid line and — for powder E33

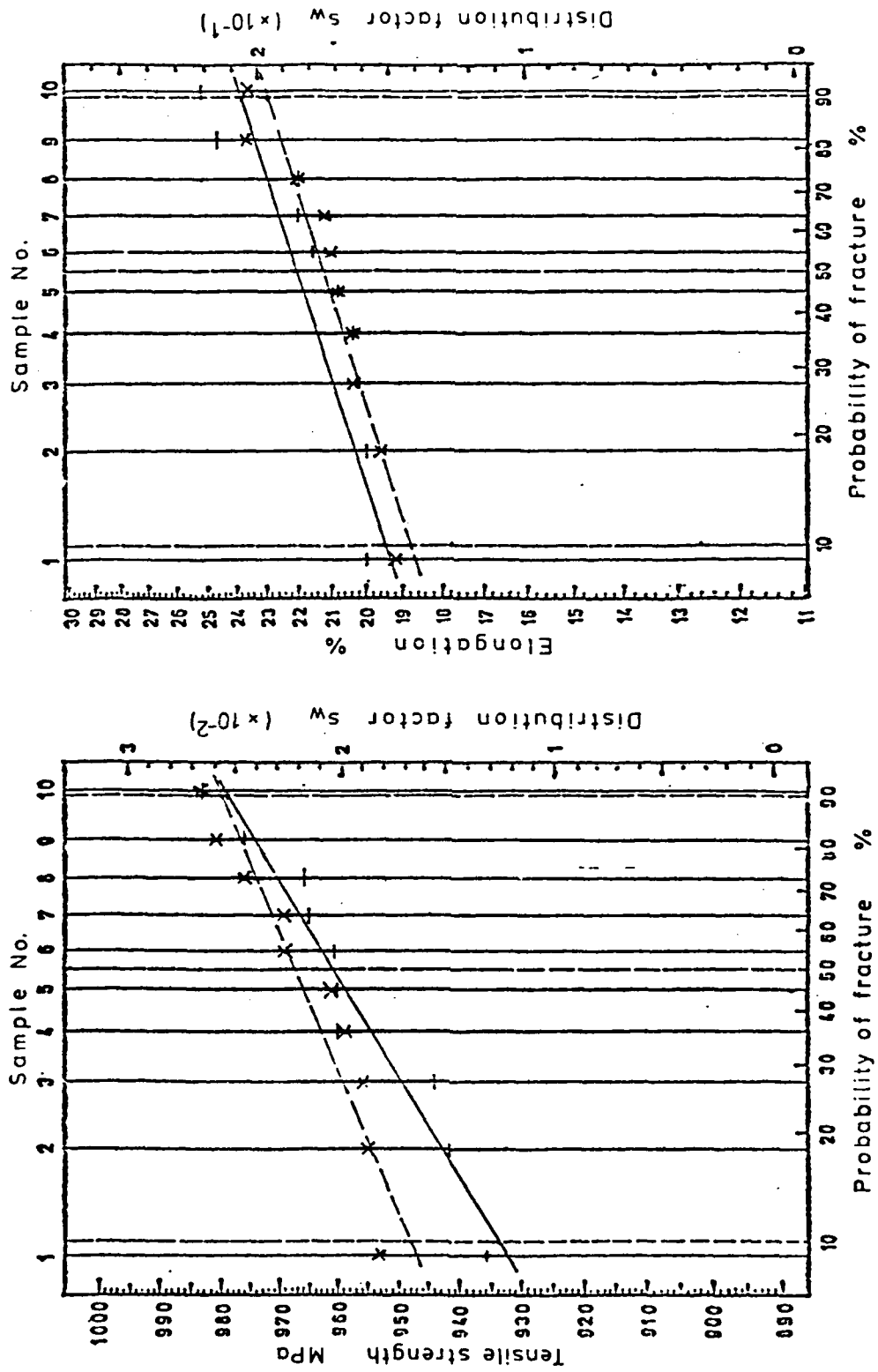broken line and x for standard powder W503

Powder E36 (100 ppm Na)

Table 22: Mechanical properties of nonporous samples
prepared from E36 and of the comparison
samples from 503

		E 36				503			
ST °C	TP °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1485	2 1	17,0808	937	21,4	288	17,0652	951	19,8	287
		17,0580	942	21,6	282	17,0607	940	21,4	292
		17,0733	954	21,6	291	17,0635	951	22,0	288
		17,0707	941	23,6	287	17,0639	960	22,2	295
1485	2 1	17,0621	919	20,0	292	17,0539	935	19,8	287
		17,0664	929	23,6	292	17,0512	932	17,2	190
		17,0606	919	22,0	284	17,0593	939	22,8	290
		17,0743	918	23,0	290	17,0609	925	16,0	287

Mean values $\pm$ standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_B MPa	δ %
E 36	11,80 $\pm$ 0,03	17,07 $\pm$ 0,01	30,9	287 $\pm$ 5	932 $\pm$ 13	22,1 $\pm$ 2,1
503	11,70 $\pm$ 0,01	17,06 $\pm$ 0,01	31,4	289 $\pm$ 3	941 $\pm$ 9	20,2 $\pm$ 2,3

Table 23: Mechanical properties of porous samples
prepared from E36 and of the comparison samples
from 503

| ST TP | E 36 | | | | 503 | | | |
^{o}C ^{o}C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1495 4	16,1606	8o3	8,o	284	17,o629	929	22,o	287
	15,1484	798	4,9	270	17,o552	917	23,o	235

Powder E39 (50 ppm Na)

Table 24: Mechanical properties of the samples prepared
from E39 and of the comparison samples from 503

| ST TP | E 39 | | | | 503 | | | |
$^{\circ}C\ ^{\circ}C$	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
	16,9037	884	1o,8	281	17,o412	953	22,4	295
1480 2 -1	16,9293	916	14,o	283	17,o27o	955	2o,o	29o
	16,8o23	926	1o,8	278	17,o635	976	22,o	295
	16,7796	92o	11,2	284	17,o639	96o	22,2	3o3

Mean values ± standard deviations

	ρ_{Cr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_B MPa	δ %
E 39	11,64 ± o,o3	16,85 ± o,o7	3o,9	281 ± 3	911 ± 19	11,7 ± 1,5
5o3	11,7o ± o,o1	17,o5 ± o,o2	31,4	296 ± 5	961 ± 1o	21,7 ± 1,1

Powder E45 (50 ppm Li)

Table 25: Mechanical properties of the samples prepared from E45 and of the comparison samples from 503

ST TP	E 45				503			
°C °C	ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
1480 3 +	17,0929	963	23,0	292	17,0333	951	23,6	290
	17,0855	944	22,4	297	17,0295	967	24,0	295
	17,0817	949	23,2	290	17,0433	966	22,4	292
	17,0456	965	22,4	288	17,0180	951	23,0	287
1485 4 +	17,0801	968	22,4	286	17,0372	952	21,8	292
	17,1045	960	24,2	280	17,0451	949	21,6	282
1485 3 +	17,1105	956	23,2	285	17,0466	954	21,6	286
	17,0918	945	21,8	290	17,0197	956	22,2	291
	17,0563	949	22,0	286	17,0183	945	21,8	296
	17,0669	954	21,2	287	17,0263	948	22,6	291

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_{50} MPa	s_σ .10⁻²	δ_{50} %	s_δ .10⁻²
E 45	11,98 ± 0,02	17,09 ± 0,02	29,9	288 ± 5	956	0,861	22,7	3,614
503	11,70 ± 0,01	17,03 ± 0,01	31,3	290 ± 4	955	0,681	22,5	3,398

Fig.39: Weibull Diagrams for powder E45
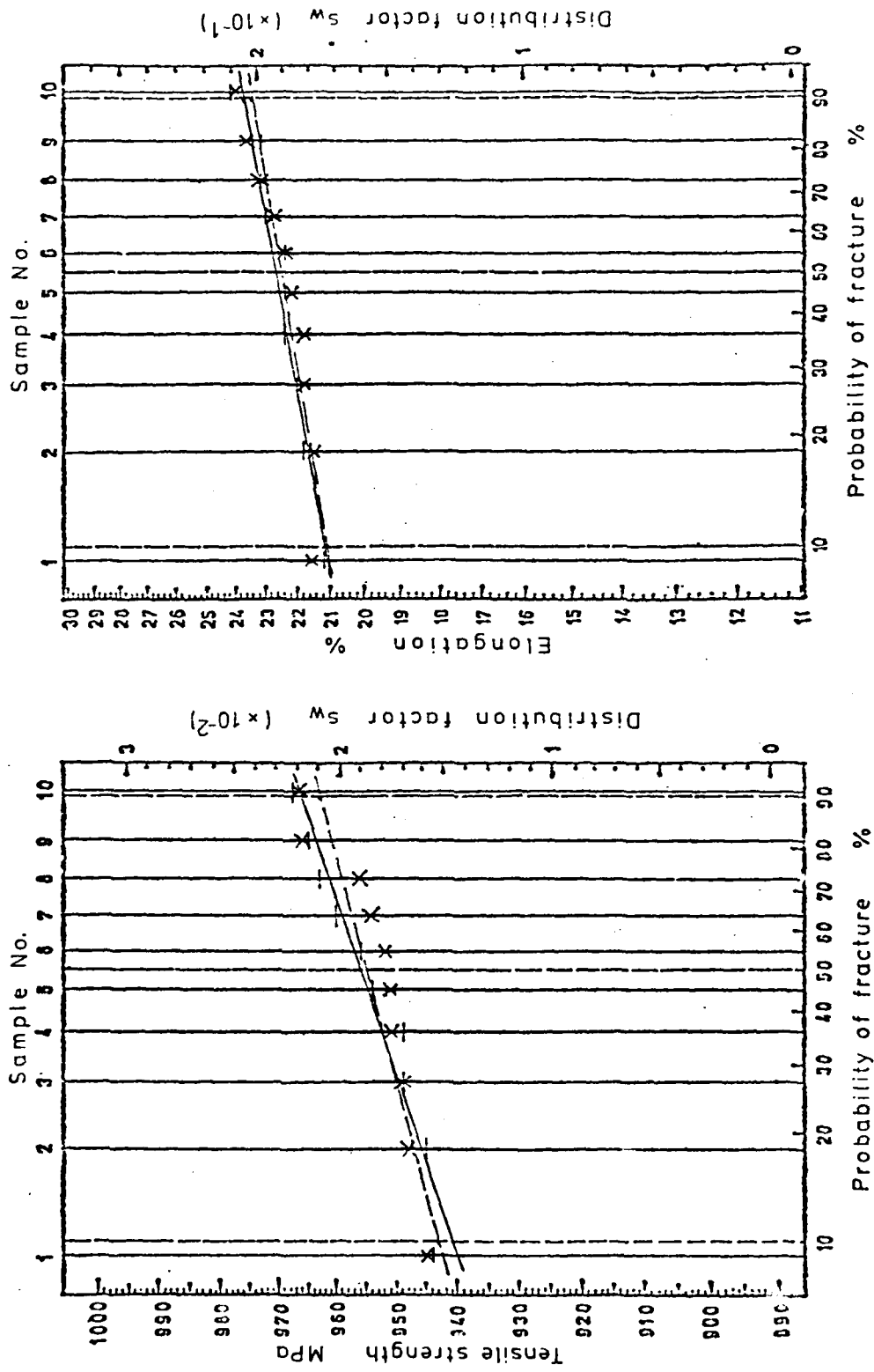
solid line and — for powder E45

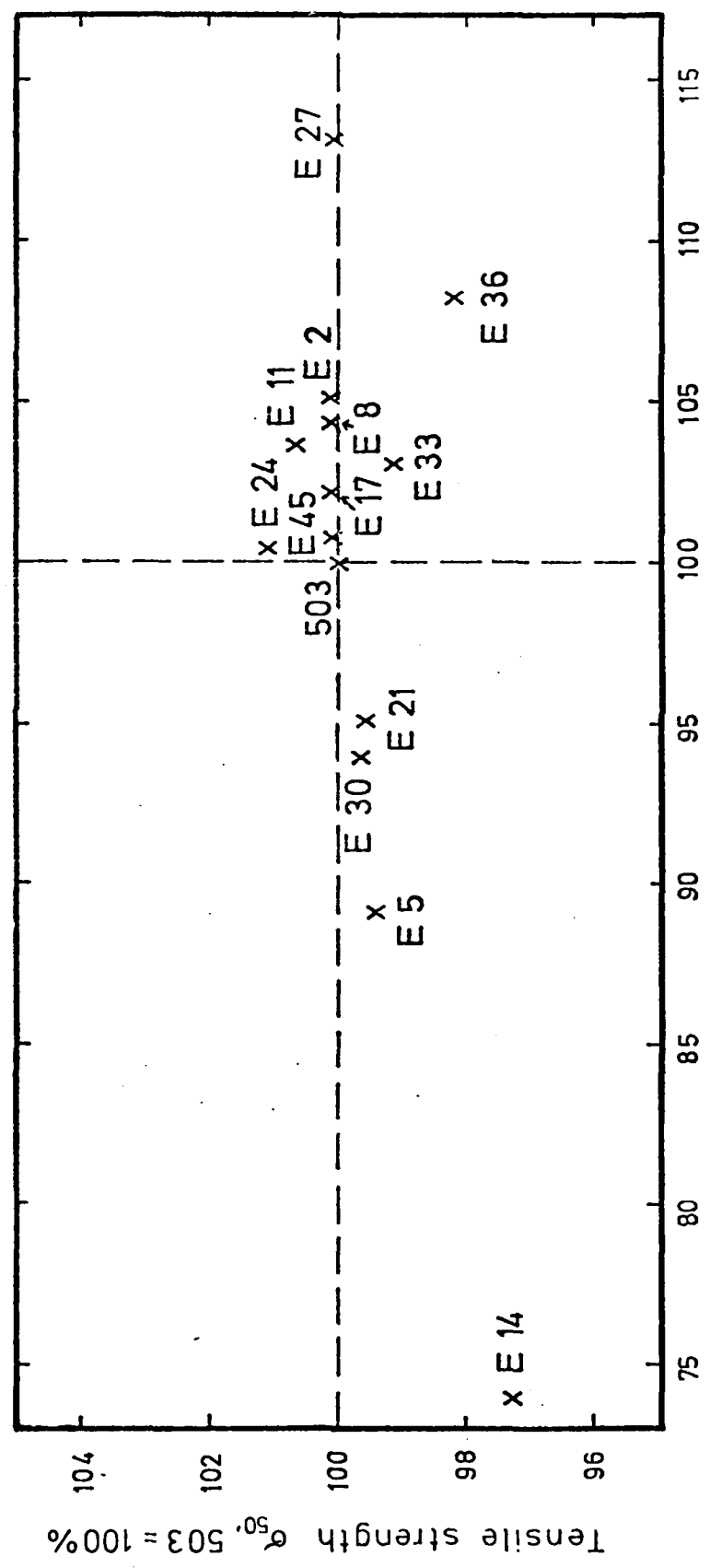broken line and x for standard powder W503

Fig.40: Comparison of σ_{50} and δ_{50} of all powders used

As is clearly shown by the tables and especially the
Weibull-diagrams, all mechanical properties are
excellently reproducible, even the elongations, which
are very sensitive to even minor change in the sintering
conditions. This becomes most evident when comparing
the properties of standard samples prepared from W503/79
which were sintered in different test series; both
the absolute values and the slope of the Weibull straight
line are relatively constant, indicating a reproducibility
of the results, even over a period of several months.
The samples prepared from doped powders show a similarly
narrow scatter for the individual values. Only the
tensile strength scatter is in a few cases somewhat
different, but no fixed trend is discernible. Against
this background, the results of the experiments appear
very reliable.

The difference in tensile strength and elongation between
doped and standard samples are shown to advantage in Fig.
Here σ_{50} (the stress which would cause 50% of the samples
to break) and δ_{50} of the differently doped heavy metals
are shown, σ_{50} and δ_{50} of the standard samples being
taken as 100% and the deviations of σ_{50} and δ_{50} of
doped samples from those of the standard are shown for
all doped powders. This diagram shows clearly that most
 doped powders result in very much the same mechanical
properties for the heavy metals as the standard powders.
Only E27, containing 100 ppm U, causes a marked increase
in elongation; maybe U forms chemical compounds with impurities
thus removing embrittling elements from W, while on the
other hand samples sintered from E14 (250 ppm Al) show
considerable decreases in ductility; probably layers of
Al_2O_3 on the surface of the W grains (see Fig. 6) inhibit
wetting between grains and binder. The only really important

influence was observed on samples prepared from E36 and
E39 containing Na; the samples were extremely swollen
and were interlaced with pore channels.With E36 some
faultless samples could be prepared that could also
be tested. From samples sintered from E39, however,
no meaningful results could be attained because the
high porosity of the samples caused not only low
mechanical properties but also a very wide scatter
in the individual values, which could be regarded as
more or less random.

Metallographic sections were prepared from all the types
of heavy metals investigated. The microhardness of the
binder and the W-grains were measured by counting the
grains on strips 0,6 mm long; on each section 9 strips
were counted and the average was calculated. The values
thus gained are only relative, but for comparison purposes
very reliable because of the excellent reproducibility.

Neither microhardness nor mean grain size show a definite
relationship to the mechanical properties. For the heavy
metal, with U however there is a very good coincidence in
that these heavy metals, which were most ductile of all,
showed a very small grain size and also a high microhardness
especially of the binder. This according to Holtz (8)
is essential for obtaining good elongations. With other
powder, however, such a relationship is not evident.

These experiments have shown that in general W heavy metals
are not extremely sensitive to different qualities of
W powders, with the exception of a few elements, which
should be contained in very small quantities (e.g. Al) or
as chemical compounds not volatile at sintering temperatures
(Na). This seems to be confirmed by the results of the
experiments with E30W; the powder contains much more Na

than E36 and E39 but gives faultless samples, apparently
due to the Na being bound as NaF. Both absolute values
and reproducibility of the mechanical properties of
heavy metals sintered from doped powders are quite
comparable, and sometimes better, than those of the
undoped standard samples.

Table 26: Microhardness and mean grain size of W heavy
metals prepared from different W powders

| W powder | Microhardness (20g boad) | | mean grain size |
	W grains	binder	(um)
E2	391	301	19,5
E5	404	331	21,3
E8	411	309	19,5
E11	411	329	20,7
E14	396	318	19,9
E17	421	363	22,2
E21	465	369	18,0
E24	401	357	19,3
E27	465	363	17,4
F30	411	319	17,0
E33	373	319	21,3
E36	424	314	19,0
E39	411	319	18,5
E45	422	341	20,8
503	392	336	19,8

SUMMARY :

The principal aim of this project, to gain improved
knowledge about the influence of fabrication parameters
and impurities in the raw materials on the properties
of W heavy metals with a composition of 90 wt% W, 6,7 wt% Ni
and 3,3 wt% Fe was reached in two steps. During the first
year, thorough investigations into the influence of grain
size and grain size distribution of the W powders on
the compactibility of the W-Ni-Fe powder mixtures showed
W powders of ~ 3 μm to be optimal. Compactibility was
improved most by adding 1% camphor as a pressing lubricant.
The sintering tests revealed that thorough pre-reduction
of the green samples before sintering inhibited the extreme
brittlemess that can appear when   oxidized powders are
used and led to excellent and very reproducible mechanical
properties. Slow cooling in the furnace after sintering
almost doubled the obtained elongation.

SEM photos clearly showed the fundamental difference between
non-reduced and pre-reduced samples:
The non-reduced samples exhibited only intergranular
fracture, the binder phase being torn away from the W grains
quite easily. Pre-reduction treatment very much improved
the interphase strength between W grains and binder. The
fracture in these samples ran indisciminately through
grains and binder, most being clear cases of transgranular
fracture.

Evaluation of the sintering parameters showed that at a
temperature of $\sim 1470^{\circ}$C and a sintering time of 30 min
the optimum combination of mechanical properties was
obtained. As was shown by grain size investigations on
metallographic samples, longer sintering times and, to a
lesser degree, higher sintering temperature cause unwelcome
grain growth. From a sintering series comprising W heavy
metals with 95 and 97% W it was determined that with
these compositions temperatures of at least 1490°C

for an optimal 30 min sintering time were necessary to obtain complete density. Sintering under these conditions resulted in elongations of 13% and 4% respectively as compared to a typical 24% with 90% specimens.

During the second year the investigations concentrated mainly on the influence of W powder chemistry on the properties of the heavy metals. A large series of experiments was carried out to show definitely the difference between the powders. The samples were sintered under the optimum sintering conditions, and in the individual batches samples prepared from standard W 503/79 powder were sintered in at least 3 batches, thus permitting a meaning-ful statistical evaluation. Besides the usual Gaussian statistics, Weibull statistics already well established in many fields of technology and suitable for fracture analyses were selected. As with heavy metals tensile strength and elongation are usually directly connected, both were evaluated in this way, and the Weibull statistics showed the excellent reproducibility achieved in these experiments. For the entire test series, the values of the standard samples sintered in different batches remained nearly constant and for both doped and standard samples the scatter of the individual values in the batches was very nearrow. With this foundation reliable conclusions about the effect of impurities in W were possible.

The comparison of the different powders revealed that most doped powders result in mechanical properties very similar to those of standard samples; U is somewhat advantageous, but Al lowers the elongation considerably. Only Na as Na_2O really causes detrimental effects, resulting in very porous samples with accordingly low tensile strength and elongation. Na in non volatile compounds, e.g. NaF, Na_2O. $.SiO_2$, however seems to be harmless.

From these tests it can be concluded that heavy metals
are not very sensitive to small amounts of impurities
in the starting W powders if certain elements are
removed or are contained as harmless compounds. The
selection of W powders for the production of heavy metals,
therefore, seems to be a not very critical step in
production of these alloys as for as chemical purity
and trace impurities are concerned. It is however
important as for as other properties, as grain size,
agglomerates or grain size distribution are concerned.

Investigations into the influence of small amounts of
other metals added to the Ni-Fe-binder did not result
in improvements of the properties. The samples doped
with V were very swollen and porous and accordingly
exhibited very low mechanical properties and also poor
reproducibility. Although the reproducibility of the
other series was quite comparable to that obtained with
standard samples, in only a few cases were the absolute
values of the standard samples reached.

Thorough evaluation of the individual steps of the sintering
cycle made it clear that the bake out of the pressing
lubricant is not critical as long as a certain rate of
de-waxing is maintained. At too low a temperature, the
camphor reacts with the metal powders and the resulting
carbides embrittle the sintered samples. Because of its
vital importance, the pre-reduction treatment was thoroughly
investigated. The optimum temperature for pre-reduction
is between 1000° and $1200^{\circ}C$; at lower temperatures, the
reduction rate is too low, at higher temperatures, the
pores close too rapidly and the H_2 cannot penetrate the
bars to reduce them completely. Tests with pre-oxidized
samples confirmed the effectiveness of the pre-reduction

by raising the temperature from 500 to 1400°C over a
period of 6 hrs. Even strongly oxidized samples showed
excellent properties after the sintering cycle. Extremely
slow cooling of the samples from sintering temperature
to 1415°C did not result in improvements over samples
conventionally cooled in the furnace.

Heat treatments which were performed in H_2 at various
temperatures and with various cooling rates resulted
in embrittlement of the samples cooled rapidly after
sintering while the samples cooled slowly reached
satisfactory properties; with heat treatment in N_2,
however, the cooling rate was of no importance for the
properties of the samples. This effect indicated that
hydrogen embrittlement and not intermetallic phase
precipitates in the binder is responsible for the
brittleness of the rapidly cooled samples. Slow cooling
removes the H_2 as a vacuum heat treatment. Sophisticated
heat treatments after sintering therefore are not essential;
apparently the same effect can be achieved by cooling the
samples slowly after sintering.

As final result of this work it can be stated that
the influence of the sintering parameters is much more
pronounced than that of the purity of the starting W
powders, if they are in the normal range of a good high
quality industrial product. For both absolute values and
reproducibility of the mechanical properties, deviations
from the optimum sintering cycle can do more harm than
impurities in the W-powders. During production, therefore,
control of the sintering process seems to pay off more
than the purchase of extremely pure, and expensive, W powder.

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SAMPLE IDENTIFICATION E 5 W

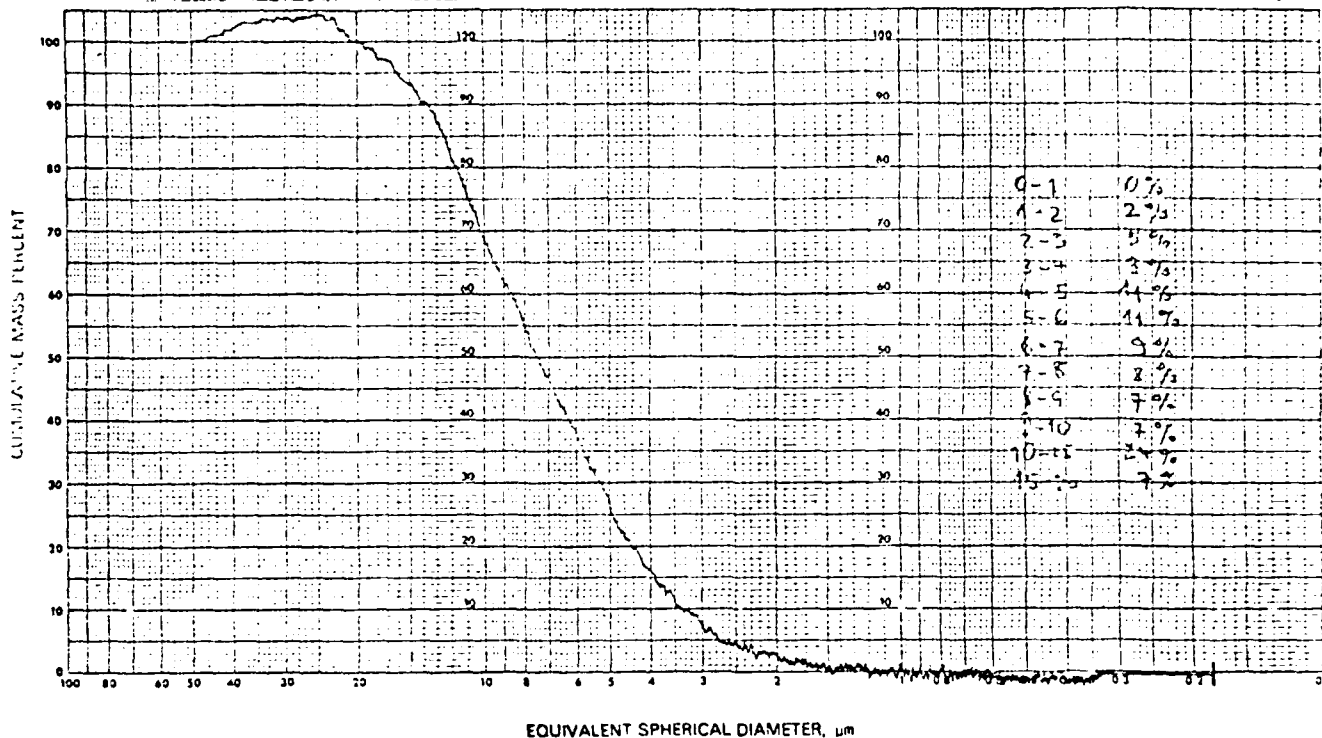Density 19,3 g/cc LIQUID Sedispose A-13 Density _____ g/cc Viscosity _____ cp

Preparation 60' deagglomeviant + 15' US

DATE 79-04-30

BY PH

TEMPERATURE 28 °C

RATE 529 START DIA 50 µm

0-1	0%
1-2	2%
2-3	5%
3-4	3%
4-5	11%
5-6	11%
6-7	9%
7-8	8%
8-9	7%
9-10	7%
10-15	27%
15-20	7%

EQUIVALENT SPHERICAL DIAMETER, µm

micromeritics

SAMPLE IDENTIFICATION E 2 W

Density 15,3 g/cc LIQUID Sedispose A-13 Density _____ g/cc Viscosity _____ cp

Preparation 60' deagglomeviant + 15' US

DATE 79-05-02

BY RH

TEMPERATURE 27 °C

RATE 558 START DIA. 50 µm
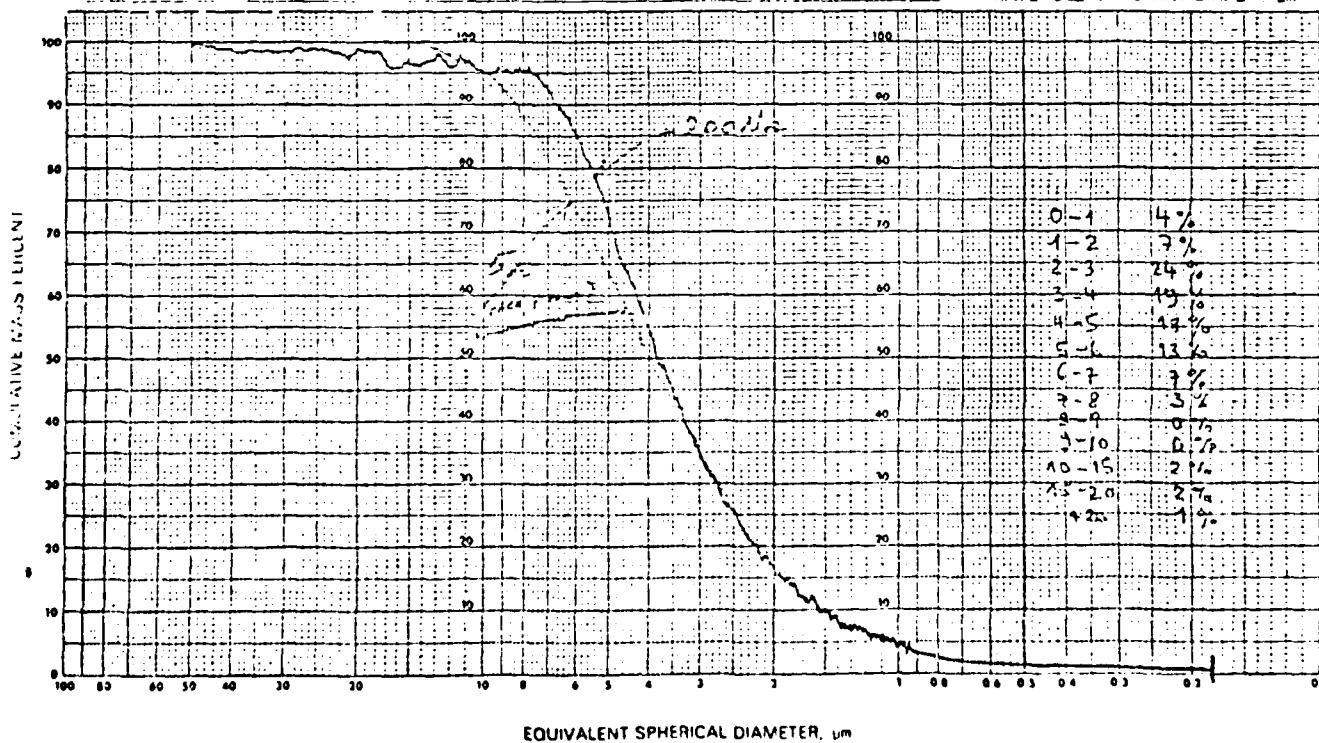
0-1	4%
1-2	7%
2-3	24%
3-4	19%
4-5	13%
5-6	13%
6-7	7%
7-8	3%
8-9	0%
9-10	0%
10-15	2%
15-20	2%
+20	1%

EQUIVALENT SPHERICAL DIAMETER, µm

micromeritics

SAMPLE IDENTIFICATION E 11 W

Density 19,3 g/cc   LIQUID Sedisperse A - 13 Density _____ g/cc   Viscosity _____ cp

Preparation 60' deagglomerial + 15' US

DATE 79-05-02
BY RA
TEMPERATURE 29 °C
RATE 597   START DIA 50 µm

0-1	23 %
1-2	28 %
2-3	21 %
3-4	15 %
4-5	9 %
5-6	3 %
6-7	1 %

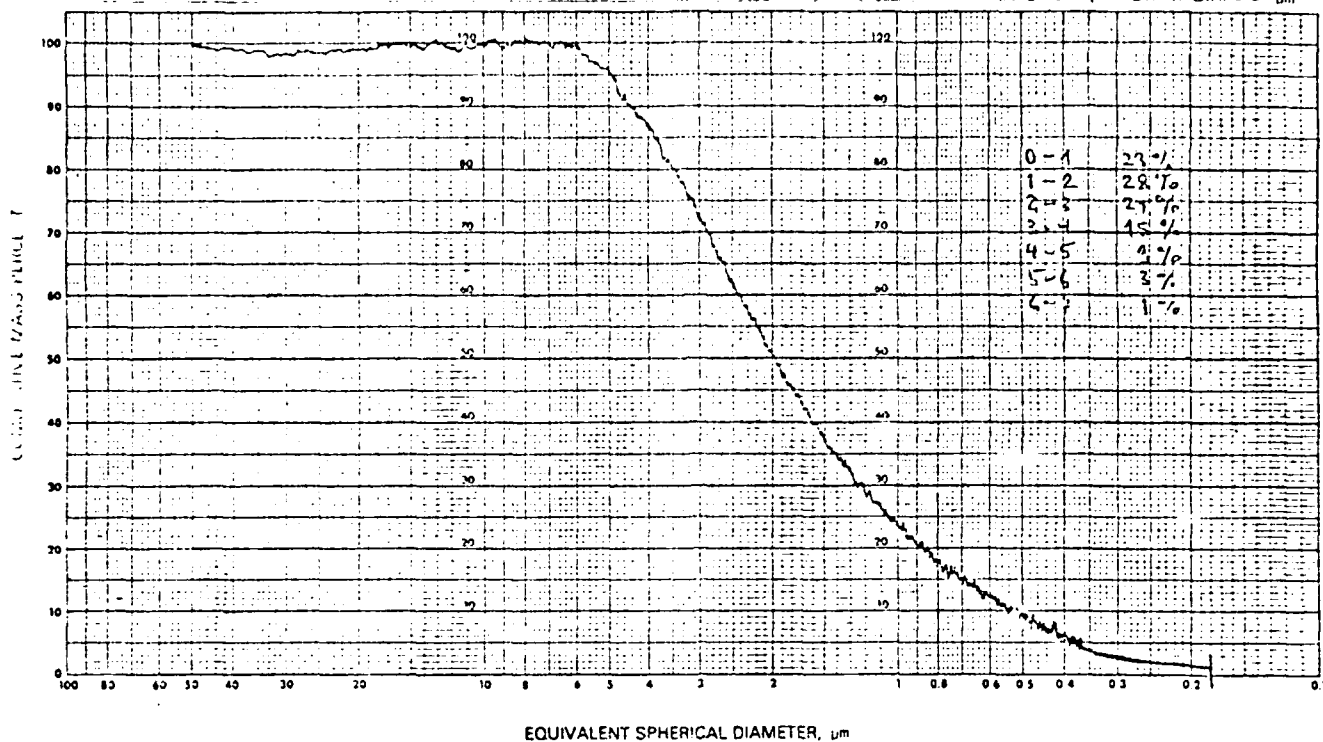EQUIVALENT SPHERICAL DIAMETER, µm

micromeritics

SAMPLE IDENTIFICATION E 8 W

Density 19,3 g/cc   LIQUID Sedisperse A-B Density _____ g/cc   Viscosity _____ cp

Preparation 60' deagglomerial + 15' US

DATE 79-05-02
BY RA
TEMPERATURE 29 °C
RATE 597   START DIA 50 µm

0-1	12 %
1-2	28 %
2-3	27 %
3-4	15 %
4-5	10 %
5-6	5 %
6-7	2 %

EQUIVALENT SPHERICAL DIAMETER, µm
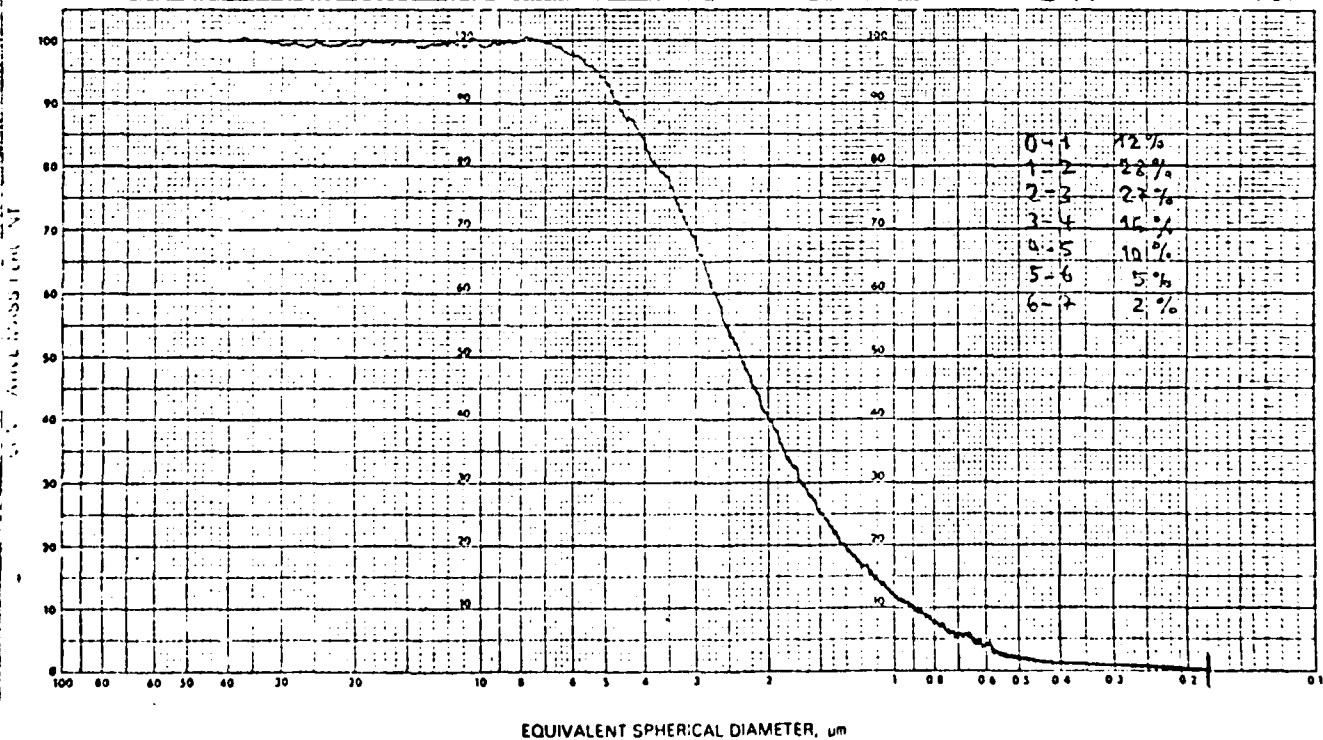
micromeritics

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION   E 14 W

Density 19,3 g/cc   LIQUID SEDISPERSE A-B Density _____ g/cc   Viscosity _____ cp

Preparation   60' deagglomeried + 15' US

DATE 79-05-02

BY RA

TEMPERATURE 30 °C

RATE 616   START DIA. 50 um

0-1	24 %
1-2	24 %
2-3	19 %
3-4	14 %
4-5	10 %
5-6	6 %
6-7	3 %

EQUIVALENT SPHERICAL DIAMETER, μm

micromeritics
instrument corporation

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION   E 17 W

Density 19,3 g/cc   LIQUID SEDISPERSE A-B Density _____ g/cc   Viscosity _____ cp
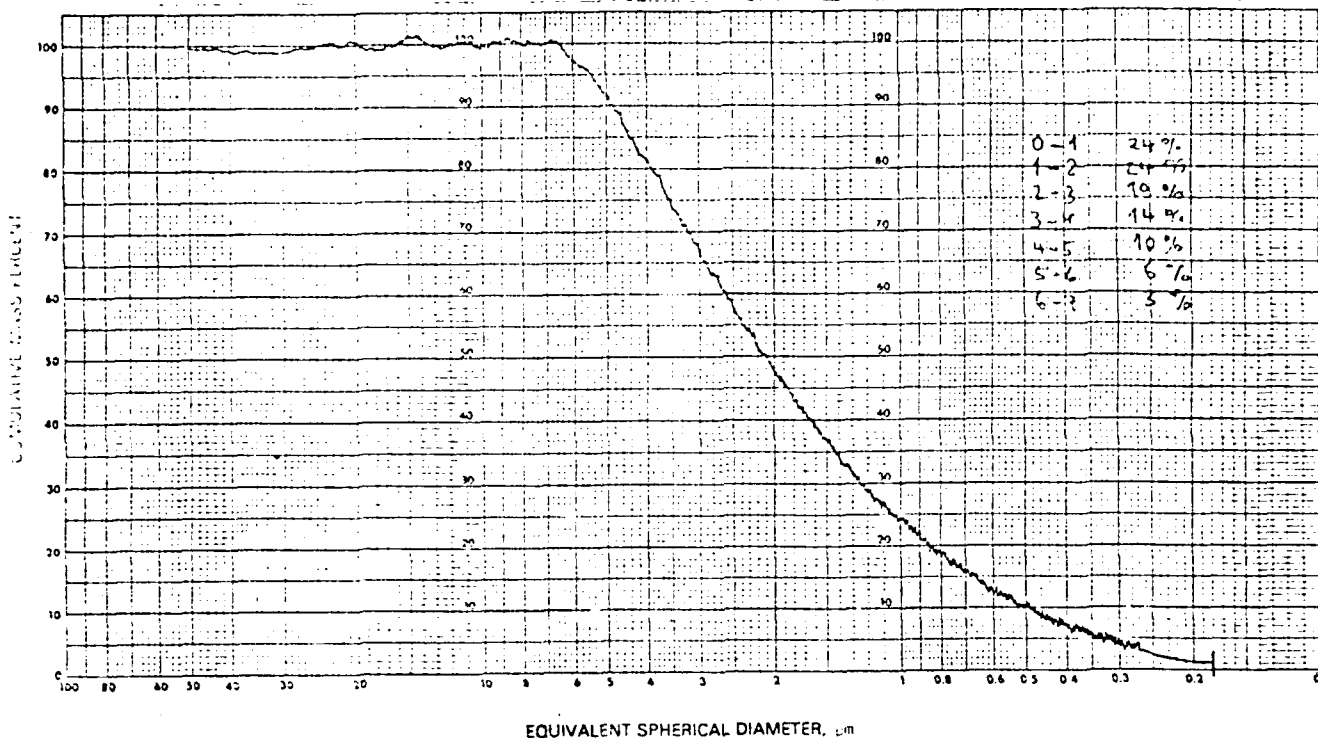
Preparation   60' deagglomeried + 15' US

DATE 79-04-11

BY Koenig

TEMPERATURE 30 °C

RATE 616   START DIA. 50 um

0-1	12 %
1-2	22 %
2-3	25 %
3-4	16 %
4-5	10 %

CUMULATIVE MASS PERCENT

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION ___ E 24 W ___

Density _19.3_ g/cc   LIQUID _SEDISPERSE A-13_ Density ___ g/cc   Viscosity ___ cp

Preparation _60' deagglomeration + 15' US_

DATE _79-09-11_

BY _Kouiazg_

TEMPERATURE _33_ °C

RATE _679_   START DIA _53_ µn

EQUIVALENT SPHERICAL DIAMETER

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION ___ E 21W ___

Density _19,3_ g/cc   LIQUID _SEDISPERSE A-13_ Density ___ g/cc   Viscosity ___ cp

Preparation _60' deagglomeration 15' US_

DATE _79-09-11_

BY _Kouiazg_

TEMPERATURE _32_ °C

RATE _659_   START DIA _50_ µn

EQUIVALENT SPHERICAL DIAMETER, µn
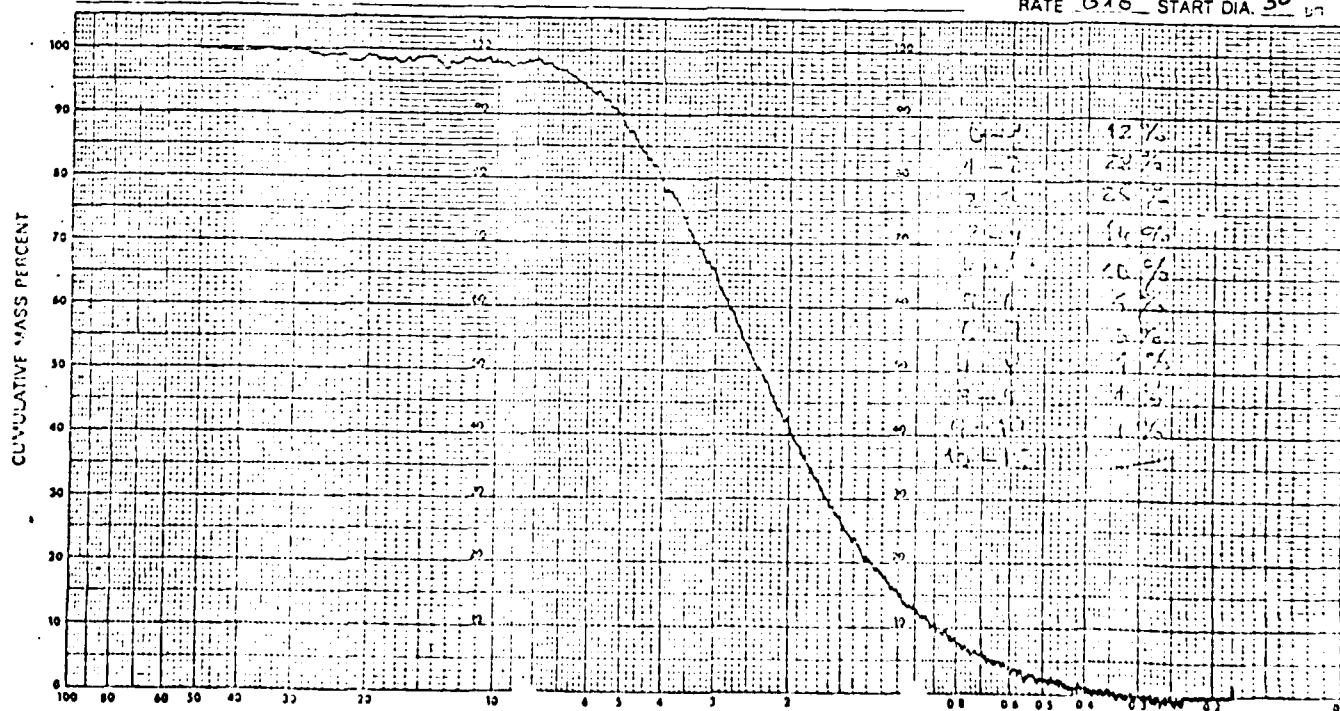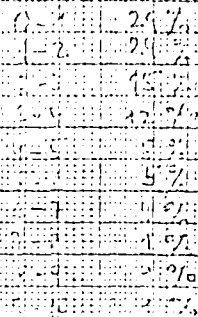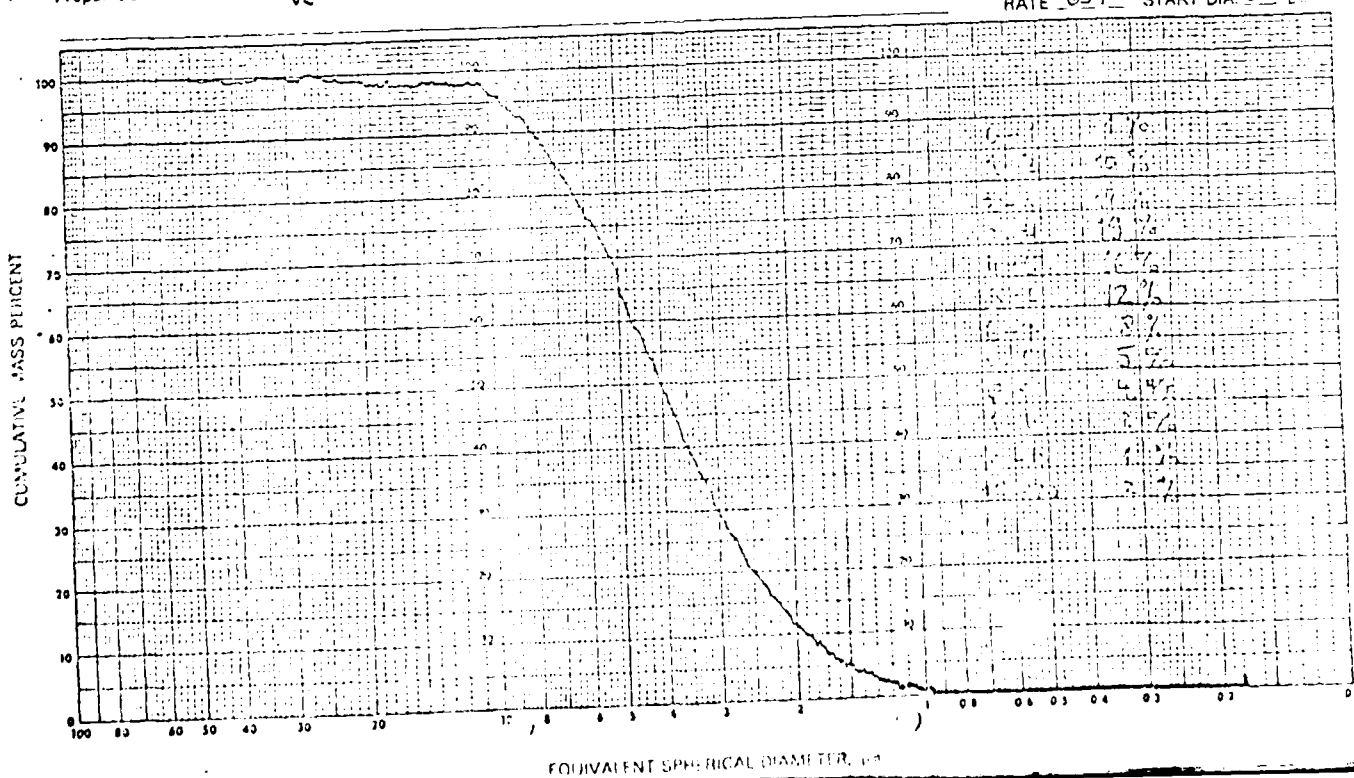
PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 30 W

Density 19,3 g/cc LIQUID SEDISPERSE A-13 Density ___ g/cc Viscosity ___ cp

Preparation 60' deagglomerial + 15' US

DATE 79-04-30

BY RW

TEMPERATURE 31 °C

RATE 657 START DIA 50 µm

0-1   2 %
1-2   43 %
2-3   19 %
3-4   23 %
4-5   20 %
5-6   12 %
6-7   4 %
7-8   2 %
8-9   2 %
9-10 1 %
10-15 2 %

EQUIVALENT SPHERICAL DIAMETER, µm

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 27 W

Density 19.3 g/cc LIQUID SEDISPERSE A-13 Density ___ g/cc Viscosity ___ cp

Preparation 60' deagglomerial + 15' US

DATE 79-09-11

BY Knigg

TEMPERATURE 33 °C

RATE 679 START DIA 50

CUMULATIVE MASS PERCENT

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION _E 36 W_   DATE _79-04-12_

Density _19.3_ g/cc   LIQUID _SEDISPERSE A-13_ Density _____ g/cc   Viscosity _____ cp   BY _Krieg_
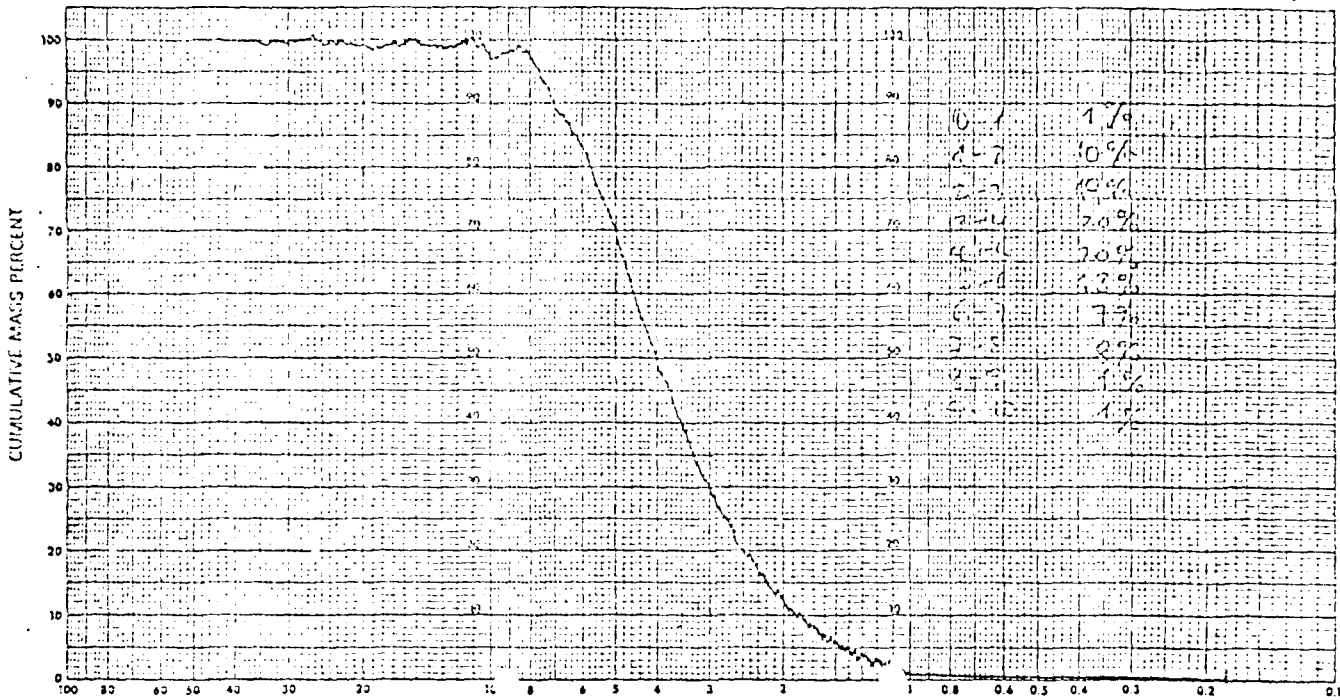
Preparation _60' deagglomeriert + 15' US_   TEMPERATURE _28_ °C

                                                                 RATE _579_   START DIA _50_ µr

0 - 1	1 %
1 - 2	10 %
2 - 3	10 %
3 - 4	20 %
4 - 5	20 %
5 - 6	12 %
6 - 7	7 %
7 - 8	2 %
8 - 9	1 %

CUMULATIVE MASS PERCENT

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION _E 33 W_   DATE _79-04-30_

                                                                 BY _RA_

Density _14.3_ g/cc   LIQUID _SeDisperse A-13_ Density _____ g/cc   Viscosity _____ cp
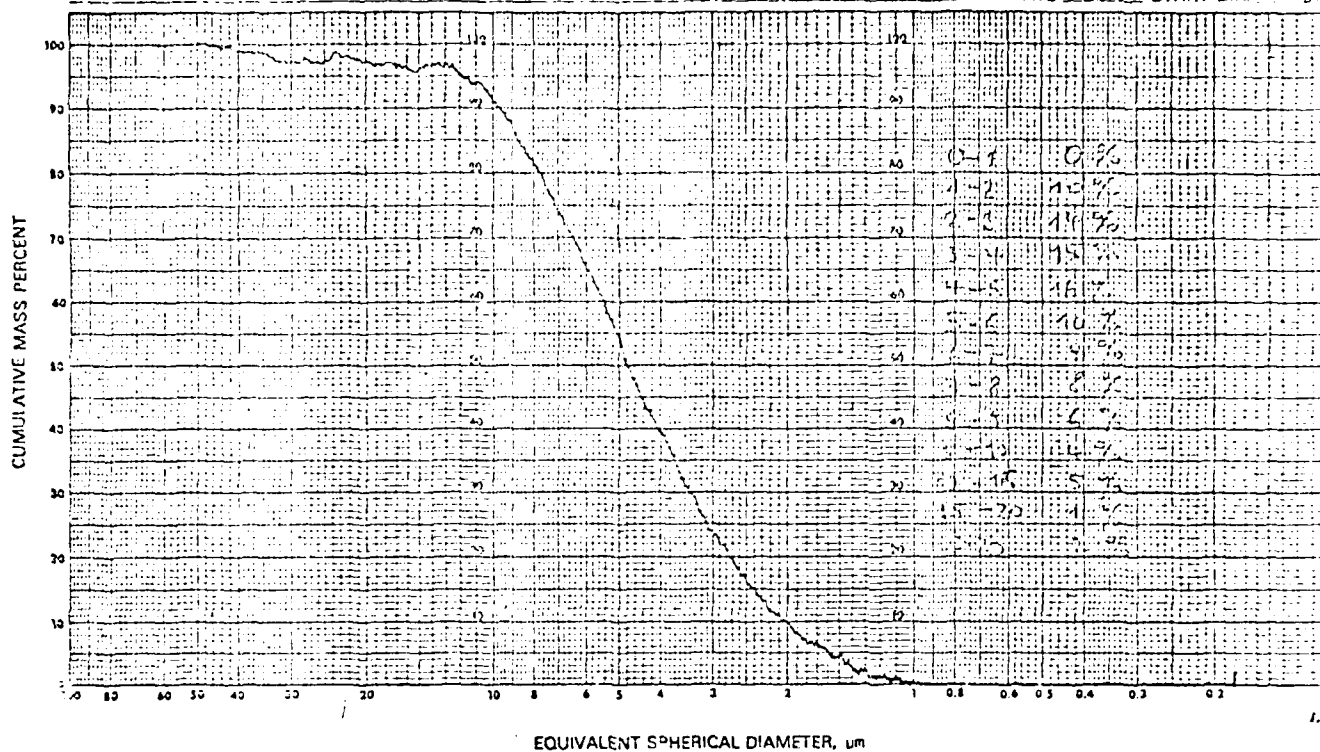
Preparation _60' deagglomeriert + 15' US_   TEMPERATURE _30_ °C

                                                                 RATE _616_   START DIA. _50_ µm

0 - 1	18 %
1 - 2	25 %
2 - 3	20 %
3 - 4	15 %
4 - 5	10 %
5 - 6	6 %
6 - 7	4 %
7 - 8	1 %
8 - 9	1 %

EQUIVALENT SPHERICAL DIAMETER, µm

micromeritics

Density _19.3_ g/cc LIQUID _SEDISPERSE A_ Density ____ g/cc Viscosity ____ cp   BY ____ Kowiegg

Preparation _60' deaggl. + 15' US_   TEMPERATURE _33_ °C

RATE _679_ START DIA _50_ µm

CUMULATIVE MASS PERCENT

EQUIVALENT SPHERICAL DIAMETER, µm
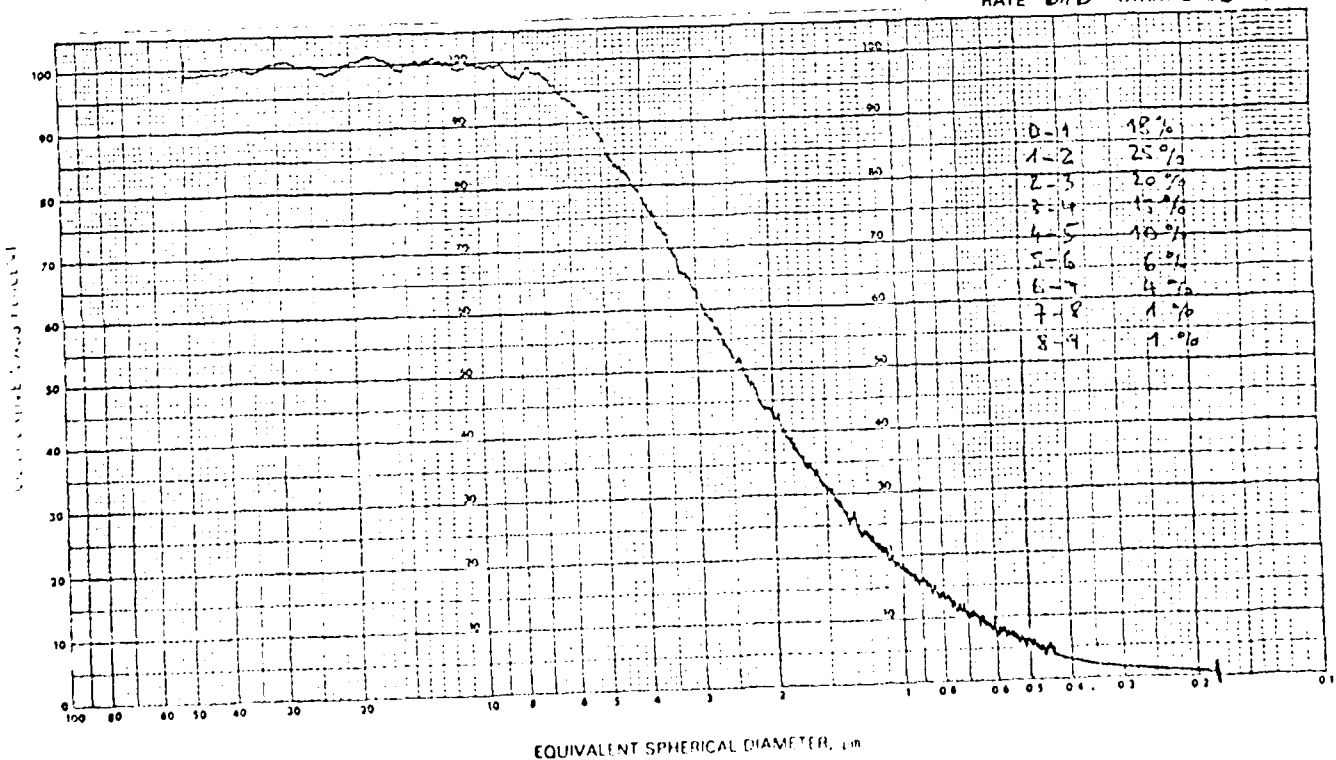
micromeritics
instrument corporation
5680 goshen springs road · norcross georgia 30093

Form 500?

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION _E 39 W_   DATE _79-09-12_

Density _193_ g/cc LIQUID _SEDISPERSE A·B_ Density ____ g/cc Viscosity ____ cp   BY _Kowiegg_

Preparation _60' deaggl. + 15' US_   TEMPERATURE _32_ °C

RATE _659_ START DIA _50_ µm

CUMULATIVE MASS PERCENT

EQUIVALENT SPHERICAL DIAMETER, µm

SAMPLE IDENTIFICATION 503 /79 WB D .... ( )   DATE 79 - 04 -05

Density 19,3 g/cc   LIQUID SEDISPERSE H-B Density ___ g/cc   Viscosity ___ cp   BY RH

Preparation 60' desagglomerient + 15' US
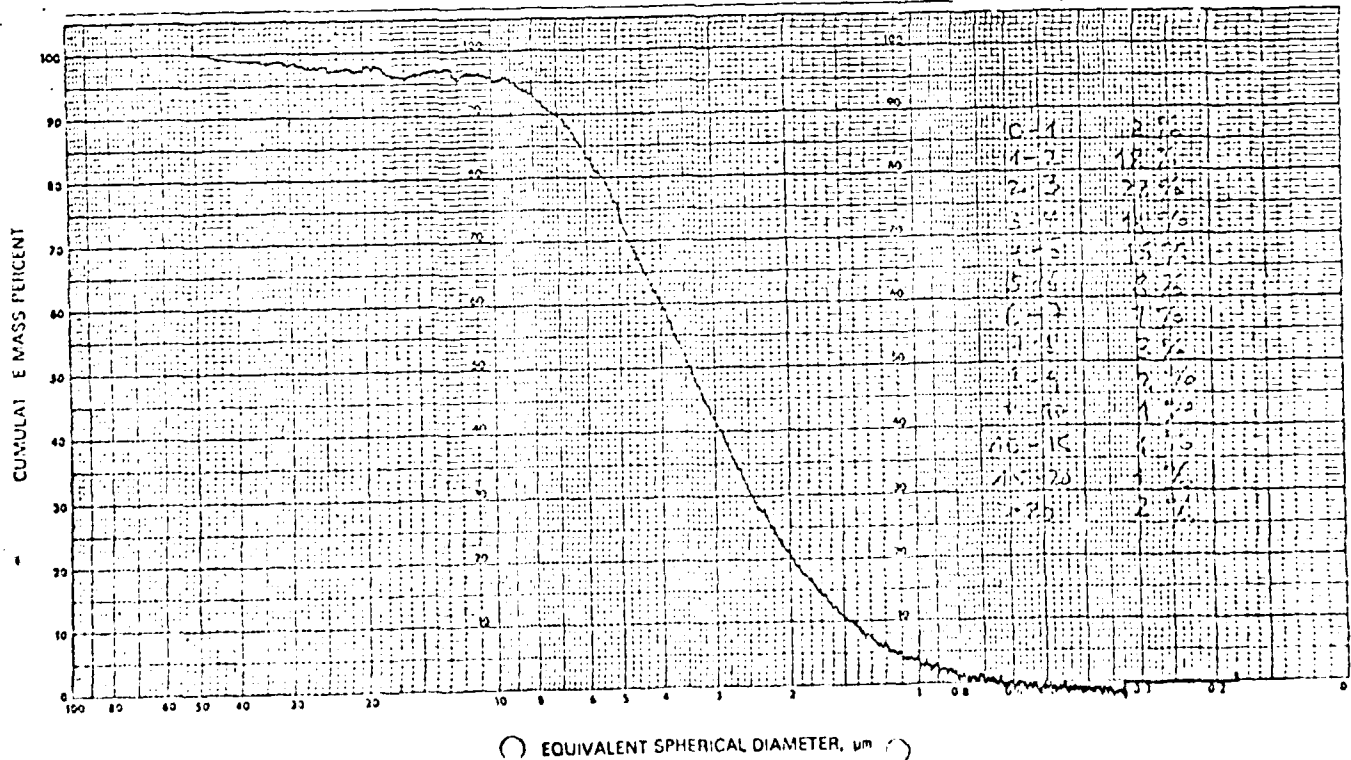
TEMPERATURE 30 °C

RATE 59% START DIA. 50 µm

CUMULATIVE MASS PERCENT

EQUIVALENT SPHERICAL DIAMETER, µm

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instrument corporation

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